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REACTIVE SPUTTER DEPOSITION OF VANADIUM, NICKEL, AND MOLYBDENUM
OXIDE THIN FILMS FOR USE IN UNCOOLED INFRARED IMAGING

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Yao Jin

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The dissertation of Yao Jin was reviewed and approved* by the following:

Mark W. Horn  
Professor in Engineering Science and Mechanics Department  
Dissertation Advisor  
Chair of Committee

Thomas N. Jackson  
Robert E. Kirby Chair Professor in Electrical Engineering Department

S. Ashok  
Professor in Engineering Science and Mechanics Department

Michael T. Lanagan  
Professor in Engineering Science and Mechanics Department

Judith A. Todd  
P. B. Breneman Department Head Chair  
Head of the Department of Engineering Science and Mechanics

*Signatures are on file in the Graduate School
ABSTRACT

A vanadium oxide (VO$_x$) thin film is the most common imaging layer used in commercial uncooled focal plane arrays for infrared cameras. These VO$_x$ thin films have an $x$ value ranging from 1.3 to 2 and have low resistivity (0.1 to 10 $\Omega\cdot$cm), high temperature coefficient of resistance (TCR) (−2 to −3%/K), and low 1/f noise. Reactive ion beam sputtering is typically used to deposit these VO$_x$ thin films for commercial thermal imaging cameras. However, the reactive ion beam deposition system for the VO$_x$ is reported to have less than desirable throughput and a narrow process window.

In this work, the potential for reactive pulsed-dc magnetron sputtering of nanocomposite VO$_x$ thin films for microbolometer applications was investigated. VO$_x$ thin films with resistivity from $10^{-4}$ to $10^5$ $\Omega\cdot$cm with a TCR from 0 to −4.3%/K were deposited by reactive sputtering from a metallic vanadium target in argon/oxygen mixtures with substrate bias. Magnetron sputtered VO$_x$ shows bolometric properties comparable to those of commercial-grade IBD prepared VO$_x$. Important limitations for manufacturing implementation of reactive magnetron sputtering such as hysteresis oxidation and non-uniform oxidation of the vanadium target surface were evaluated. The VO$_x$ film deposition rate, resistivity, and temperature coefficient of resistance were correlated to oxygen to argon ratio, processing pressure, target-to-substrate distance, and oxygen inlet positions. To deposit VO$_x$ in the resistivity range of 0.1−10 $\Omega\cdot$cm with good uniformity and process control, it was found that a lower processing pressure, larger target-to-substrate distance, and an oxygen inlet near the substrate are useful. Other processing methods employing magnetron sputtering were investigated such as co-sputtering of V and V$_2$O$_3$ target, sputtering from a VC target, a V$_2$O$_5$ target, and a V$_2$O$_x$ target but initial investigation of these methods did not yield a superior process to the simple sputtering of a pure metallic vanadium target.
Another technique, biased target ion beam deposition (BTIBD), was investigated for deposition VO\textsubscript{x} thin films with potential alloy additions. In this BTIBD system, ions with energy lower than 25 eV were generated remotely and vanadium targets are negatively biased independently for sputtering. High TCR (<-4.5%/K) VO\textsubscript{x} thin films have been reproducibly prepared in the resistivity range of 10\textsuperscript{3}-10\textsuperscript{4} Ω•cm by controlling the oxygen partial pressure using real-time control with a residual gas analyzer. These high resistivity films may be useful in next generation uncooled focal plane arrays for through-film rather than lateral thermal resistors. This architecture could improve the sensitivity through the higher TCR without increasing noise normally accompanied by higher resistance. Processing parameters necessary to produce high TCR VO\textsubscript{x} films and details on how this novel deposition tool operates are discussed. Addition of molybdenum and its effects on the VO\textsubscript{x} thin films’ electrical properties were also studied.

Using the BTIBD system, VO\textsubscript{x} films in the resistivity range of 0.1-10 Ω•cm desired for current microbolometer application were difficult to produce. Pure molybdenum oxide (MoO\textsubscript{x}) and nickel oxide (NiO\textsubscript{x}) thin films were deposited by reactive biased target ion beam deposition and evaluated in a search for materials with a larger process latitude. MoO\textsubscript{x} thin films were deposited with resistivity from 3 to 2000 Ω•cm and with TCR from -1.7 to -3.2 %/K. NiO\textsubscript{x} thin film were deposited with resistivity from 1 to 300 Ω•cm and with TCR from -2.2 to -3.3 %/K. The thermal stability of these films was also investigated. It was found that biased target ion beam deposited high TCR MoO\textsubscript{x} and NiO\textsubscript{x} thin films are polycrystalline semiconductors and have good stability in air. Compared to commonly used VO\textsubscript{x} thin films, MoO\textsubscript{x} or NiO\textsubscript{x} thin films may offer improved process control for resistive temperature sensors and a superior deposition rate. However, preliminary experiments indicate that these films might have relatively higher 1/f noise.
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Chapter 1

Introduction

Infrared (IR) imaging is one of the main methods used in night-vision devices. The IR radiation emitted from biological objects is in the range of 8-14 μm and can be detected by two kinds of detectors: photon and thermal detectors.[1] A photon detector is based on the interaction between incident photons and a sensing material’s electrons. In order to reduce the noise effect caused by thermally generated carries and recombination, a photon detector is cooled by a bulky cooling system. Thermal detectors are based on a change in material property as a function of temperature caused by IR radiation. Thermal detectors can be based on thermoelectric effects, pyroelectric effects, and a change in resistivity with temperature [2]. The focus of this research is based on the resistive thermal detectors.

1.1 Microbolometers and Figures of Merit

Resistive microbolometers are thermal detectors with a sensing material that experience a change in resistance when absorbing incident IR radiation. A pixel of the device is freestanding and thermally isolated from the readout integrated circuitry (ROIC) by “standing” on a composite structure containing the electrically conductive legs. Figure 1-1 shows the schematic of a typical microbolometer pixel design. A microbolometer pixel typically includes a thin layer of sensing material (either metal or semiconductor), IR absorbing film, and an infrared reflecting layer below the active sensing layer to increase infrared absorption. The microbolometer pixel absorbs the IR and results in a temperature change, hence altering the sensing material resistance. The
change of resistivity is then detected by read-out circuitry in either the current or voltage signals through the metal legs. [2]

![Figure 1-1. The schematic of a microbolometer pixel. [3]](image)

In order to maximize the sensitivity of the pixel, the sensing material temperature coefficient of resistance (TCR) should be high. A metal thin film has a low, positive TCR whereas a semiconductor thin film has a TCR that is negative and significant, in the -1 to -6 % range. Eq.1-1 and 1-2 give the definition of the TCR value:

\[
%TCR = \frac{-E_a}{(k_B T_{room})^2} \times 100\%
\]

\[E_a = \frac{d(lnR)}{d(1/k_BT)}\]

where \(E_a\) is the thermal activation energy, \(k_B\) is Boltzmann constant, and \(T_{room}\) is room temperature (25°C) [2].

In order to reduce the power consumption during the operation, a lower resistance is often desired. Hence, a low room temperature resistivity sensing materials with high TCR should
be used. However, the sensing materials used for microbolometers are often limited by the noise of both the material and the read out circuitry being implemented. Four types of noise are seen in electrical properties: 1/f noise, Johnson noise, temperature fluctuation noise, and background fluctuation noise (Eq.1-3).

\[ V_{\text{total}}^2 = V_{\text{Background}}^2 + V_{\text{Temperature fluctuation}}^2 + V_{\text{Johnson}}^2 + V_{\text{1/f}}^2 \quad \text{Eq. 1-3} \]

Of the four types of noise listed above, temperature fluctuation noise and background noise are related to the device design. The Johnson noise and 1/f noise (pink noise) are based on the material. For semiconductors, 1/f noise is often thought to be due to carriers trapping and untrapping, which is a predominant noise at low frequency (1 Hz to 1 kHz). The 1/f noise is given by:

\[ V_{\text{1/f}} = (kV_{\text{bias}}^2/f)^{1/2} \quad \text{Eq. 1-4} \]

where \( f \) is the frequency that the noise is measured, \( V_{\text{bias}} \) is the bias applied during measurement, \( k \) is the 1/f noise parameter.

Johnson noise, on the other hand, is not dependent on frequency, and is attributed to free electrons random motion in a resistor:

\[ V_{\text{Johnson}} = (4k_BTRB)^{1/2} \quad \text{Eq. 1-5} \]

where \( k_B \) is the Boltzmann constant, \( T \) is measurement temperature, \( R \) is the total resistance of the pixel structure, and \( B \) is the noise bandwidth given \( B= \frac{1}{2\Delta t} \) and \( \Delta t \) is the pulse bias duration.

Reducing the total resistance \( R \) can decrease the Johnson noise of a microbolometer. The 1/f noise is strongly dependent on the microbolometer resistor properties such as material, processing parameters, contact qualities, and so on [3]. In low frequency devices, 1/f noise can be higher than the Johnson noise, and become the dominating factor to limit the microbolometer sensitivity.
The responsivity $R$ is one of the figures of merit that determines the effectiveness of microbolometer devices. $R$ is a measure of the ability of the infrared device to convert IR to a useful signal, given by the following equation:

$$R = \frac{\alpha \eta i_b \beta R_b}{G} \quad Eq.1-6$$

where $\eta$ is the emissivity, $i_b$ is the bias current, $\alpha$ is the TCR of the sensing material, $R_b$ is the resistance, $\beta$ is the areal fraction of the detector array covered by an active sensing material, and $G$ is the thermal conductance of the supporting legs.

Another important figure of merit is the noise equivalent temperature difference (NETD), which describes the minimum temperature difference that can be detected by a microbolometer. NETD is related to the optical structure of device, read out circuitry, and sensing materials.

$$NETD \propto \frac{\text{Noise}}{\text{TCR}} \quad Eq.1-7$$

In order to minimize NETD to get the highest resolution, the total noise should be minimized and the responsivity should be maximized [2].

### 1.2 Vanadium oxide thin films as microbolometer sensing materials

Many materials have been investigated as the thermally active materials for resistive microbolometers. Metal thin films have been investigated as resistive microbolometers due to their CMOS (complementary metal-oxide-semiconductor) compatibility. Titanium is the most widely used metal for microbolometers. The TCR of titanium thin film is reported to be 0.26%/K. A 64×64 Ti based microbolometer array detector with a pixel size of 75×75 µm has production cost as low as $100 [4]. Though metal films have low noise and low cost, the low TCR limits its performance. High TCR semiconductor materials have been investigated as resistive
microbolometers, such as: VO$_x$, [3],[5], hydrogenated amorphous Si (a-Si) [6],[7], yttrium barium copper oxide (YBaCuO) [8], and nickel oxide (NiO$_x$) [9], [10]. Among these materials, VO$_x$ and a-Si based microbolometers have approximately 70% and 17% of the uncooled infrared imaging market share, respectively [11]. VO$_x$ thin films have relatively low resistivity (0.1 to 10 Ω•cm) and high TCR (-2 to -3 %/K), whereas a-Si have relatively high resistivity (200 to 2500 Ω•cm) and higher TCR (-2.5 to -3.9 %/K) [3],[5],[7]. Both VO$_x$ and a-Si based microbolometer pixel size reaches 17×17 μm$^2$, with NEDT about 50 milliKelvin [4],[11].

VO$_x$ of various compositions for microbolometers has been prepared by many deposition methods, such as reactive ion beam deposition (IBD) [3], [5], reactive radio frequency (rf) sputtering [12], reactive dc sputtering [12], [13], and pulsed laser deposition (PLD) [14], [15]. However, vanadium has multiple valence states (+5,+4,+3,+2) and it can transition from one phase to another very quickly under different oxygen levels. This makes extremely difficult to fabricate single stable phases of VO$_x$ thin films. Many vanadium oxide phases show metal-insulator transitions (MIT) at different temperatures such as V$_2$O$_3$, VO$_2$, and Magneli phases of VO$_x$ which are between V$_2$O$_3$ and VO$_2$ as shown in Figure 1-2 [16]. The Magneli phases are described by V$_{n}$O$_{2n-1}$ and n is an integer [17]. VO$_2$ is semiconducting at room temperature and then changes to metallic when temperature is higher than 68°C [18]. The MIT temperature for V$_2$O$_3$ is 168 K (-105°C) [17]. This drastic change in resistivity increases the responsivity of devices. However, the operation of the device requires a cooler and heater, which make V$_2$O$_3$ and VO$_2$ not suitable for uncooled microbolometers. In addition, the fast resistivity change may not be easily controlled by the readout circuitry. V$_2$O$_5$ is one of the most stable phases of VO$_x$. The resistivity for V$_2$O$_5$ is between 1E2 to 1E6 Ω•cm depending on the structure [19]. Though the TCR of V$_2$O$_5$ could be as large as -4.4 %/K (amorphous) [20], V$_2$O$_5$ is not suitable for the targeted resistivity range for pulse-biased microbolometer usage due to its high resistivity [2].
Figure 1-2. Phase diagram of VO$_x$ system [16].

The VO$_x$ thin films for microbolometers originally deposited by IBD have no phase transition near room temperature. The room temperature resistivity of VO$_x$ prepared by IBD is from 4E-3 to 1 Ω·cm with TCR ranges from -0.65 to -3.5 %/K [21]. As shown in Figure 1-3 [3], higher TCR VO$_x$ films inevitably show higher room temperature resistivity. The ideal x value of VO$_x$ for microbolometer usage is between 1.75 and 2 [22], [23]. The deposited VO$_x$ thin film properties can be largely influenced by deposition techniques and processing parameters. The deposited films should also exhibit good thermal and electrical stability.
Figure 1-3. IBD prepared VO$_x$ linear relationship of TCR vs. resistivity in log scale [3].

1.3 VO$_x$ for microbolometers deposited by different fabrication methods

When used as microbolometer sensing materials, the VO$_x$ thin films deposition temperatures should not exceed 400°C due to the monolithic fabrication of microbolometer bridge structure on silicon readout circuitry [24].

Since the Honeywell patented VO$_x$ prepared by reactive IBD method for microbolometers [25], IBD has been exclusively used to produce VO$_x$ for commercial use. Wang et al. used reactive IBD to fabricate VO$_x$ thin films with sheet resistance about 32 K Ω/sq and TCR -2.5 %/K [26]. A different Wang group [23] used IBD to deposit VO$_x$ thin film that consisted of V$_2$O$_5$ and VO$_2$ with a sheet resistance of 50K Ω/sq and a TCR of -2.1 %/K. The post annealing in Ar at 400°C caused the VO$_x$ films to show a nonlinear relationship of log resistivity
versus temperature. Chain prepared VOₓ by reactive ion beam deposition with different substrate temperature. The result shows that with increasing of substrate temperature, the deposited film grain size increases, which is consistent with the Thornton’s structure zone model [27]. Chain also investigated the change in the VOₓ thin film structure and optical properties when varying oxygen content in the reactive ion beam deposition with a metallic V target [28]. When the oxygen was low, the VOₓ changed from an FCC crystal structure to a mixed oxide phase containing VO₂. As the concentration of oxygen was increased further, the VOₓ became a mixed oxide with V₂O₅ and the grain orientation changes from preferential to randomly oriented. The oxygen content, ion beam energy and substrate temperature were found to have a great influence on the deposited VOₓ composition and structure prepared by reactive IBD.

Deposition methods such as reactive rf sputtering and reactive dc sputtering are also investigated to produce VOₓ for microbolometer usage. Luo et al. used reactive dc sputtering to prepare VOₓ thin films and followed with in-situ thermal oxidation. The films as deposited were amorphous and after in-situ annealing in oxygen, they become nano-VO₂ with average grain size of 19 nm. The calculated TCR as deposited was -2 %/°C and after 10 min of annealing, it increased to -3.1 %/°C [29]. Lv et al. used facing V targets dc reactive sputtering to prepare VOₓ thin films for microbolometer sensing materials [30]. The as-deposited VOₓ had a room temperature sheet resistance of 30-80K Ω/sq and a TCR above -4.5 %/°C. After being annealed in vacuum at 400 °C for 3 hours, the sheet resistance decreased to 20K Ω/sq but the TCR was still as high as -4.4 %/°C. X-ray photoelectron spectroscopy (XPS) spectra show that the annealing in vacuum makes the V₂O₅ dissociate and results in large amounts of V⁴⁺ and V⁺, which the authors attribute as the cause of the increase of conductivity.

VOₓ thin films have also been prepared by pulsed laser deposition (PLD) using a V₂O₅ target at room temperature. Though the prepared films have a high TCR of about -2.8%/K but the room temperature resistivity was as high as 1000 Ω•cm which makes it unsuitable for
microbolometer device sensing materials [31]. Due to the difficulty of controlling the fabrication of the VO\textsubscript{x} composition and phase, a multilayer structure consisting of V\textsubscript{2}O\textsubscript{5} and V was prepared by reactive magnetron rf sputtering at room temperature without oxygen. The as-deposited multilayer VO\textsubscript{x} thin films were further annealed at 300°C to make the oxygen diffuse from the V\textsubscript{2}O\textsubscript{5} to the metallic V layer. By adjusting the thickness of the V and V\textsubscript{2}O\textsubscript{5} thin films, the VO\textsubscript{x} resistivity varied from 4-30 Ω•cm with TCR from -1.8%/K to -2%/K [32].

In 2006, Penn State was awarded a multidisciplinary university research initiative (MURI) supported by The Army Research Office to investigate sensing materials for uncooled microbolometers. VO\textsubscript{x} thin films for infrared imaging have been prepared by magnetron pulsed dc reactive sputtering method, [13], [33]–[37] and show similar or even superior properties compared to VO\textsubscript{x} prepared by IBD as shown in Figure 1-4 [35].

The Penn State group determined that the desired VO\textsubscript{x} thin films’ microstructure in the interested resistivity and TCR range is a nanocomposite, where there are FCC VO\textsubscript{x} (0.8<x<1.3) nanocrystalline domains embedded in an oxygen rich VO\textsubscript{x} amorphous matrix [38]. The growth conditions in the chamber were found to have great influences on the deposited film composition and electrical properties [39]. The presence of a nano-twin structure has been observed in VO\textsubscript{x} thin films prepared by both magnetron sputtering and IBD [40]. The rf substrate self-bias applied on VO\textsubscript{x} films during deposition makes the films denser with a higher concentration of nano-twins, which is more similar to IBD prepared samples. The microstructure of VO\textsubscript{x} deposited by different methods is shown in Figure 1-5. Enhanced electrical properties of VO\textsubscript{x} prepared with substrate bias were also reported [36]. Without substrate bias, the as-deposited films are porous; however, post-deposition process such as ex-situ annealing in oxygen/nitrogen, and implantation of hydrogen/helium can improve TCR and resistivity of these as-deposited VO\textsubscript{x} films [41]. In an effort to improve thermal stability and possibly TCR, transition metals have been incorporated into the VO\textsubscript{x} thin films. There were no significant effects on the films microstructure and little
improvement in the films electrical properties. However, by adding the transition metals in VO\textsubscript{x} thin films, the thermal stability of deposited films was improved [37].

![Figure 1-4. TCR vs. room temperature resistivity for VO\textsubscript{x} films that were prepared by different deposition methods [35].](image)

Besides VO\textsubscript{x}, our group at Penn State University also investigated other materials for microbolometer applications, such as: hydrogenated silicon (Si:H) [42], polycrystalline SiGe [43], nickel magnetite (NiMnO\textsubscript{x}) [44][45]. The bolometric properties such as: resistivity, TCR, and 1/f noise of these materials prepared by different deposition techniques are compared.
Figure 1-5. Bright field TEM pictures of VO₅ prepared by different deposition methods: ion beam deposition, unbiased magnetron sputtering, and biased magnetron sputtering [35].

Table 1-1 lists resistivity, TCR, and 1/f noise comparison of these microbolometer sensing materials. The 1/f noise and TCR are related, and the general rule is higher TCR materials have higher resistivity and 1/f noise. As shown in Eq. 1.7, in the same TCR range, lower 1/f noise is needed to get higher NETD. At TCR range from -2 to -2.5 %/K, IBD and biased magnetron sputtered VO₅ have lower 1/f noise. At TCR range from -3 to -4 %/K, a-Si and PECVD nanocrystalline and amorphous Ge:H show lower 1/f noise. However, high TCR (< -4.5% /K) VO₅ thin films have not yet been investigated, which needs to be further investigated.

1.4 Biased target ion beam deposition

In this work, a new technique: biased target ion beam deposition (BTIBD) is investigated and used to deposit microbolometer-sensing materials. This section introduces how a BTIBD system works and summarizes the work has been reported by using this unique technique.

BTIBD combines ion beam deposition and sputter deposition. In a BTIBD system, an ion beam is remotely generated and the targets are negatively biased to promote sputtering. The energy and distribution of the ion beam is mainly dependent on the ion source since the plasma
sheath toward the negatively biased target is small [49], [50]. This allows for the independent control of the generation of ion beam and biased target sputtering. The control of the ion beam energy and sputtered species energy make this technique have the potential to have good repeatability and uniformity. The Ar+ ions generated remotely in a BTIBD system typically have energies lower than 25 eV (lower than the sputter threshold of vacuum materials). At such a low energy, the contamination that will be introduced to the deposited thin films from vacuum system and other non-biased targets can be kept to a minimum. The sputter yield for some elements as a function of incident Ar+ energy is shown in Figure 1-6, and most of these element sputtering yield is less than 0.01 when incident Ar+ ion (normal to the surface) energy is lower than 30 eV [51].
Table 1-1. Resistivity, TCR, and 1/f noise values for various microbolometer sensing materials.

<table>
<thead>
<tr>
<th>Materials (MURI)</th>
<th>Resistivity (Ω•cm)</th>
<th>TCR (%/K)</th>
<th>1/f Noise ($k \times Volume$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBD (nc+a) VO$_x$</td>
<td>0.1 to 1</td>
<td>2</td>
<td>$10^{-22}$</td>
<td>[3][36]</td>
</tr>
<tr>
<td>Magnetron sputtered (nc+a) VO$_x$</td>
<td>0.001 to 1</td>
<td>0.2 to 2.6</td>
<td>$10^{-28}$ to $10^{-22}$</td>
<td>[36], [46]</td>
</tr>
<tr>
<td>Nickel Manganite</td>
<td>630</td>
<td>2.9</td>
<td>$10^{-21}$</td>
<td>[44]</td>
</tr>
<tr>
<td>PECVD a-Si:H doped</td>
<td>100 to 3000</td>
<td>2.0 to 3.6</td>
<td>$10^{-22}$ to $10^{-17}$</td>
<td>[42]</td>
</tr>
<tr>
<td>PECVD a-Ge:H</td>
<td>12,000 to 50,000</td>
<td>2.8-5</td>
<td>$10^{-20}$ to $10^{-17}$</td>
<td>[43][47]</td>
</tr>
<tr>
<td>PECVD (nc+a)Ge:H</td>
<td>750 to 4,500</td>
<td>1.8 to 6.3</td>
<td>$10^{-20}$ to $10^{-18}$</td>
<td>[48]</td>
</tr>
</tbody>
</table>
Figure 1-6. Sputter yield for some elements: Ar ions normal to the surface [51].
Based on this novel technique, 4WAVE Inc. has built a Laboratory Alloy and Nanolayer Sputtering system (LANS) and an Ion Beam Assisted Biased Target Deposition Sputtering System (IABTD) and (as shown in Figure 1-7).

4W-LANS system used in this work has also been used to prepare thin films for different applications. Gallium nitride (GaN) has been deposited on sapphire wafers using the BTIBD technique. A mixture of Ar and N₂ was introduced on to the end hall to generate plasma. Ar flow rate was fixed at 30 SCCM and N₂ flow rate varied from 3 SCCM to 30 SCCM. The liquid Ga target was biased with -850 V for 11 µs and +10 V for 3 µs. However, the prepared GaN thin films have poor structural and optical properties [52].

Amorphous rare earth substituted Bismuth Iron Garnet was also prepared by reactive sputter deposition using four metallic targets: Bi, Dy, Fe and Al in 4W-LANS system. The target voltage was -850 V with pulse width/period of 3 µs /14 µs. The composition of the BiDyFeAlO₁₂ garnet films was calculated by the single-metal oxide deposition rates with certain oxygen partial pressure from 1E⁻⁵ Torr to 5E⁻⁵ Torr monitored by a residual gas analyzer (RGA). The processing pressure was fixed at 6.4E⁻⁴ Torr. The BiDyFeAlO₁₂ garnet films were later annealed in oxygen for an hour at 650°C. After annealing, the amorphous film turned to poly-crystalline with a saturation magnetization and coercivity comparable to those films prepared by other methods [49].

4W-LANS reactive BTIBD is also used to deposit vanadium dioxide thin films. Single-phase VO₂ thin films were grown on Al₂O₃ at 450°C substrate temperature. A metallic vanadium target was used and biased with 11 µs -900 V and 3 µs +20 V. It has been found that Ar flow rate at 80 SCCM with a mixture of Ar/O₂ 80/20 gas flow rate at 5 SCCM gives the optimized growth of VO₂₅ [53]. Cr doped VO₂ thin films V₁ₓCrₓO₂ (x between 0.1 and 0.2) were also prepared by
the same group by using reactive BTIBD technique in 4W-LANS system. The films show high crystalline quality and low surface roughness [54].

A more sophisticated structure of BTIBD with a second ion source as ion assist has also been developed. The 4W-IABTD has been used to prepare: Giant magnetoresistive (GMR) multilayer spin-valves [55], diamond-like carbon(DLC) thin films corporation with Co, Ti, Ni, and W [56], [57], as well as magnetic tunnel junction(MTJ) with naturally oxidized AlOₓ barriers [58].

Figure 1-7. Schematic of (a) 4Wave IABTD system and (b) 4Wave BTIBD system [59]

In this thesis, 4W-LANS BTIBD system with off-axis geometry was used to prepare transition metal oxide thin films. More details of this system will be discussed in Chapter 2.
1.5 Thesis outline

This thesis explores the potential of reactive sputtering of VO$_x$, NiO$_x$, and MoO$_x$ thin films for microbolometer applications. In the past, ion beam deposition has been exclusively used to fabricate commercial VO$_x$ thin films for microbolometer sensing materials due to its good process controllability. However, IBD has low throughput. Our group has proven that magnetron pulsed-dc reactive sputtering of VO$_x$ with substrate bias has similar or enhanced electrical properties to IBD VO$_x$. However, there are important limitations for manufacturing implementation due to its inherent process non-uniformity. In this work, we try to answer the questions as follows:

1). Can magnetron pulsed-dc sputtering be an alternative method to IBD to prepare VO$_x$ thin films for microbolometers. Are there ways to improve process controllability and improve yield?

2). Can high TCR VO$_x$ thin films be prepared with good thermal stability and relatively low 1/f noise? How do they compare to other high TCR materials?

3). Can other sensing materials with good bolometric properties and easier process control than VO$_x$ be developed for microbolometer applications?

Chapter 2 of this thesis describes the processing and analysis methods used in this work, includes deposition techniques, thin film properties characterization, and device fabrication. The operation details of the new deposition technique (biased target ion beam deposition) are also discussed. Chapter 3 details experiments designed to evaluate the potential of magnetron reactive sputtering of VO$_x$ thin films. The process controllability was improved by varying different processing parameters such as sputtering target, processing pressure, oxygen to Ar inlet ratio, substrate bias, reactive gas inlet position, substrate to target position etc. Chapter 4 introduces the high resistivity high TCR vanadium oxide thin films prepared by reactive biased target ion beam
sputtering. The potential usage of these materials for a through-film structure microbolometer pixel was investigated. Chapter 5 describes the fabrication and characterization of high TCR nickel oxide and molybdenum oxide thin films as potential microbolometer sensing materials prepared by biased target ion beam deposition. The correlation of these film properties to processing conditions was studied. Aging tests and post-annealing effects on deposited films were also investigated. The 1/f noise of NiO\textsubscript{x} is compared to VO\textsubscript{x} thin films and other sensing materials investigated. Chapter 6 summarizes the results obtained in this thesis work and proposes possibilities for future work.
Chapter 2
Experimental Methods

This chapter includes experimental methods for depositing and characterizing the thin films studied in this thesis. In this work, metal oxide thin films were deposited by both reactive magnetron sputtering and biased target ion beam deposition using various processing parameters. Post-deposition processes such as rapid thermal annealing (RTA) were used to evaluate the metal oxide thin film thermal stability. The thin films were characterized by profilometry, spectroscopic ellipsometry (SE), grazing incident x-ray diffraction (GIXRD), Raman spectroscopy, and energy-dispersive X-ray spectroscopy (EDS). Electrical properties of deposited films were analyzed by the transmission line measurement (TLM) method.

2.1 Reactive magnetron pulsed direct current (dc) sputtering

2.1.1 Reactive magnetron pulsed-dc sputtering issues

Magnetron pulsed-dc sputtering is a physical vapor deposition method can be used to deposit electrically insulating materials directly or through a reactive sputtering process of metal targets where reaction products are electrically insulating. In conventional dc sputtering, a metallic target (cathode) has negative potential compare to the substrate and chamber walls. For pressures between 1 mTorr and 10 Torr, The potential difference causes electrons to accelerate from cathode to anode. The electron gains enough kinetic energy to sufficiently ionize the gas molecules in the chamber by inelastic collisions, which leads to a cascade process such that stable plasma is sustained. The positive gas ions (typically Ar+) then accelerate toward the cathode and when they have sufficient energy, sputter target atoms into the gas phase. The sputtered target
atoms deposit on the chamber wall and substrate. In magnetron guns, magnets are placed under the targets create a crosswise magnetic field over the cathode and largely increase the electrons travel path thereby increasing the probability of ionizing collisions by trapping electrons in orbits near the targets. Using a magnetron gun decreases the minimum pressure necessary to sustain the plasma to about 1 mTorr from something closer to 10 mTorr.

Reactive sputtering from a metal target enables compound deposition with lower target fabrication cost and higher deposition rate [60]. In reactive sputtering, the reactive gas is added to the Ar sputtering gas to form a compound film on the substrate. The deposited film composition and deposition rate is sensitive to the supply of reactive gas. In this technique, as the reactive gas supply increases, the target can become “poisoned” with an electrical insulator layer that forms on the target surface. This insulating layer then permits Ar+ ions to build-up positive charge which then repulses positive ions from further bombarding the target and decreases the sputtering rate. Pulsed-dc sputtering helps to overcome this charging issue by adding a short positive pulse to draw electrons to neutralize the charged target. A pulsed-dc bias on the target is shown in Figure 2-1: the negative portion of a duty cycle causes normal sputtering and the positive portion neutralizes the charged target.

Figure 2-1. Schematic of a pulsed-dc sputtering process. Replotted from Ref [61] and Ref [62].
In reactive sputtering with a metallic target, a process hysteresis behavior is typical, that is to say that the sputtering rate is dependent on whether or not the reactive gas flow has been increased or decreased. The hysteresis loop for deposition rate can be monitored directly by an in-situ quartz-crystal deposition-rate monitor or indirectly by measuring the cathode current/voltage on the target.

Figure 2-2 shows the hysteresis loop of the cathode voltage with constant sputtering power and partial pressure of non-reactive gas [63]. At low reactive gas flow rate, the deposited film is metal-rich. With further increasing of reactive gas flow rate, the gas-metal compound forms on the target surface and sputtering rate drops abruptly at $f_{r1}$, the sputtered film is gas-rich. By reducing reactive gas flow rate, the sputtering rate won’t increase until $f_{r2}$, where the compound layer on target surface is removed and metal is exposed. The hysteresis effect leads to process instability and should be eliminated in a manufacturing environment.

![Hysteresis Loop Diagram](image)

Figure 2-2. The hysteresis loop of reactive magnetron sputtering [63].

In addition to the hysteresis effect in reactive sputtering, there is another undesirable feature of magnetron sputtering. The magnetron introduces non-uniform sputtering of cathode due to non-uniform plasma density across the target surface. The discharge current density is
higher in the racetrack region compared to other regions. This leads to different sputtering rate across the target, which can be averaged in a non-reactive environment, but it also caused a variation in the sputtered species during reactive deposition [63]. The target sputtering rate, \( R_{\text{sput}} \), and oxidization rate \( R_{\text{ox}} \), are site-dependent across the target as shown in Figure 2-3 (a). Figure 2-3(b) shows that when reactive gas flow rate is high, \( R_{\text{ox}} \) is larger than \( R_{\text{sput}} \) and the target is covered by oxide layer (the degree of the oxide coverage \( \Theta_{\text{ox}} \) is 1). With decreasing oxygen flow rate, the oxide coverage \( \Theta_{\text{ox}} \) decreases until the racetrack of target surface has no oxide layer (the degree of the oxide coverage \( \Theta_{\text{ox}} \) is 0). When \( \Theta_{\text{ox}} \) is between 0 and 1, at the discharge region the oxide layer is continuously formed and destroyed. The \( R_{\text{sput}} \) and \( R_{\text{ox}} \) vary across the discharge region and the difference leads to possibility three different states exist simultaneously on target: fully oxidized, partially oxidized, and fully metal. The non-uniform poisoning of target may lead to non-uniformity of deposited films, both in rate and composition.

2.1.2 Experimental equipment

Some of the VO\(_x\) thin films studied in this thesis were deposited in a Kurt J. Lesker CMS-18 sputtering system. The system has three 3-inch magnetron sputtering sources and allows for substrate temperature control and RF biasing (Figure 2-4). VO\(_x\) thin films were deposited by reactive pulsed-dc magnetron sputtering from a 3-inch metallic vanadium target (99.99% V) onto 6-inch silicon wafers covered with 100 nm of thermal oxide. The deposition time was kept constant at 900 seconds. The pulsed dc power was maintained at 300 W with a 20 KHz pulse frequency and a 5 µsec pulse width using a dc magnetron power source (MDX 1000) with a SparKLE 20 pulse generator. The voltage-pulse waveform is shown in Figure 2-1. The system can accommodate 2 additional 3-inch targets which can be powered by rf power source (RFX-6000) for co-sputtering.
During all VO\textsubscript{x} film depositions in this system, a negative substrate self-bias voltage of approximately -240 V developed using 25W of 13.56 MHz RF power was used. The total gas (Ar + O\textsubscript{2}) flow rate was held at 18 SCCM with a downstream throttle valve used to adjust the deposition pressure. The target-to-substrate distance (throw distance) was set at either 4 or 8 inches by moving the target position with respect to the substrate. Oxygen with 99.99\% purity was introduced into the process chamber either near the substrate or near the target; Ar was introduced into the chamber near the target. Both the oxygen and Ar flow rates were controlled by MKS mass flow controllers. The O\textsubscript{2} to Ar (O\textsubscript{2}/Ar) inlet ratio was varied from 0.05 to 0.15. The chamber was pumped down to a base pressure of about 8E-7 Torr before each deposition.
Figure 2-3. Differential poisoning of the target around the racetrack. (a) Comparison between the normalized metal sputter rate and oxidization rate at racetrack. (b) Target is fully oxidized; the racetrack is fully covered with oxide thin film. (c) to (e) Oxide thin film layer coverage is decreasing when rO₂ is decreasing. The cathode current of target is recovered gradually back to highest value. Graph is from reference [63].
2.2 Biased target ion beam deposition

2.2.1 Biased target deposition

An alternative to magnetron reactive pulsed-dc sputtering used in this work is a novel technique called biased target ion beam deposition (BTIBD). As mentioned in Chapter 1, unlike magnetron sputtering, this technique utilizes a remote ion source to produce a low energy plasma which is then used to sputter up to three different targets simultaneously by independently applying a dc or pulsed-dc voltage to the targets. This section discusses both how the ion beam generated and how the sputtering is promoted by controlling the biased targets.

Figure 2-4. Schematic of Kurt J. Lesker magnetron sputtering system.
2.2.1.1 Low energy ion beam generation

In order to generate a low energy plasma with enough ions to illuminate the whole target, an un-focused “ion beam” is produced by a broad beam ion source. This kind of ion source requires an external electron source to produce electrons for ionization and neutralization of the ion beam. The generated electrons from the cathode-neutralizer are accelerated crossing the magnetic-field lines in the ion source anode to cause ionization. The diagram of end-hall ion beam source with a HC electron source is shown in Figure 2-5. Broad-beam ion sources include Kaufman-type gridded source and the Hall-effect gridless sources. There are two basic gridless ion sources: closed-drift ion source and end-hall ion source [64], [65]. The BTIBD systems used in this thesis was built by 4Wave Inc. and utilizes an end-hall ion source with hollow cathode (HC) electron source. Though HC is more complex than a filament source and is more expensive, the HC has much longer lifetime typically over 500 hours with noble gases. The schematic diagram of an end-hall ion source (EH1000 ion source by Kaufman and Robinson, Inc.) is shown in Figure 2-6 (a) and (b). The detailed ion source used in 4Wave BTIBD system is shown in Figure 2-6(c).
Figure 2-5. Re-plot schematic diagram of end-hall ion beam source with a HC electron source from reference [66].
Figure 2-6. (a) and (b) show cross-section schematics of end-hall ion source with grooved anode [67]; (c) shows a top-view picture of this ion source assembled with HC electron source (HCES).

As shown in Figure 2-6 (a) and (b), a permanent magnet is placed under the gas reflector. The electrons provided by HC move in circles toward to the anode due to the magnetic field at the anode, hence the probability of collision between electrons and working gas molecules increase. The ions are generated by the ion source move along the applied electrical field without influence by the magnetic field. The extra electrons produced by the HC neutralize the ions to make quasi-neutrality, where the density of electrons and ions are approximately equal in a broad ion beam. It
should be mentioned that when background pressure is below 1 mTorr, the recombination of electrons and ions is not significant [67].

The working gas to produce plasma could be a noble gas such as argon or xenon. Other working gases such as hydrogen, nitrogen, and oxygen can also be used for reactive processes. The grooved anode and the baffle are designed to reduce “poisoning” of anode from reactive gases and prevent sputtered particles from depositing on anode which is shown in Figure 2-6 (c) [67] and reducing ion current generation.

2.2.1.2 Important characterization values of the ion beam

The ion sources have non self-sustained regime and a self-sustained regime. For the self-sustained regime, the discharge voltage between anode and cathode (walls) is high enough (above 300 V) to generate electrons from conductor surfaces for ion and electron collisions. However, the non self-sustained regime, where the discharge voltage is lower, an external electron source is needed to provide electrons [68]. The BTIBD system operates the ion source at a non self-sustained regime in order to keep the ion beam at low energy (<25 eV) to prevent ions sputtering vacuum system materials. The ion beam current $I_i$ and mean value of ion beam energy $E_i$ are the most two important values for the ion beam thin film deposition.

The end-hall ion source design such as the dimension of discharge channel, magnetic field value, gas distribution system, etc. have an influence on the ion beam current as a function of discharge voltage. However, with the certain ion source (EH 1000), the processing parameters of the end-hall ion source and HC such as: emission current of HC electron source, discharge current, discharge voltage, working gas type, working gas flow rates, total processing pressure have great influences on the produced ion beam [67].
In order to keep the mean energy of the plasma as small as possible so as to reduce unwanted impurities in the film, care must be taken to choose the proper processing parameters. It has been reported that the coefficient of the ion beam energy transformation from the discharge voltage to an ion beam mean energy is related to the neutralization of the ion beam. When the ion beam is properly neutralized, whereas the emission current from an external electron source is equal to discharge current, the ion beam mean energy produced by the end-hall ion source is 60-70% of the discharge voltage with a broad energy distribution. When the emission current is lower than the discharge current, the ion beam is under neutralized, and the ion beam mean energy is only 10-50% of the discharge voltage. This coefficient will increase when the emission current is higher than the discharge current [65], [67].

In addition to the neutralization of ion beam, working gas flow rates have effects on this coefficient as well. At the discharge current, higher working gas flow rates lead to lower discharge voltage. It is reported that at the same discharge current, when discharge voltage is lower than 50 V, the increasing of discharge voltage leads to increase of ion beam current. When discharge voltage is higher than 50 V, the ion beam current does not change too much with the discharge voltage increasing, and mainly change as a function of discharge current [67].

Other values of ion beam are also important to thin film deposition, such as: ion beam divergence, distribution of ion beam energy, the coefficient of the working material utilization, the ratio of ionized particles flying into chamber to flying back into a reflector, and so on. For the end-Hall ion source, 70-80% of ions of the neutralized ion beam have a half-angle $\alpha$ of 40°-60° from the ion source axis. The large ion beam divergence enables the uniform illumination of negatively biased targets for sputtering for the system used in this thesis since the targets are 90 degrees with respect to the source axis [50], [65], [67].
2.2.1.3 Biased target deposition

In the BTIBD system, the target is negatively biased, with either direct current for conductors or pulsed dc (or rf) for dielectrics. The plasma sheath is around 2mm, which is around a few Debye lengths when pressure is about 1 mTorr. Once the target is applied with negative bias, the ions bombarding the target surface energy is the sum of ions kinetic energy $E_o$ and the potential energy gained to the target $qV_b$[67]:

$$E = E_o + qV_b$$  \hspace{1cm} Eq. 2.1

Unlike magnetron sputtering, there is no magnet under targets, so the erosion of target is uniform, and furthermore, magnetic materials (such as Ni, Fe, Co etc.) are more easily sputtered by this technique. For pure metal sputtering, the target is applied with negative dc potential. For dielectric targets and/or reactive sputtering of metal targets, pulsed dc is applied on targets for reactive sputtering.

2.2.2 Experimental equipment

A 4Wave-LANS system was used to deposited vanadium oxide, nickel oxide, and molybdenum oxide thin films. As shown in Figure 2-7, in this system, up to three 4-inch targets could be sputtered simultaneously with voltage varies from -300 to -800 V. The pulse period (full duty cycle) was 100 $\mu$sec whereas the pulse width (time duration applied with +5 V power) varied from 1-90 $\mu$sec. For vanadium oxide thin film deposition, three V targets with 99.99% purity were used for co-sputtering. For molybdenum oxide and nickel oxide thin films, a single Mo or Ni target (99.99%) was utilized.

For all the depositions, the HC Ar flow rate was fixed at 10 SCCM whereas the ion source Ar flow rate was varied from 60 to 100 SCCM. In order to keep the ion beam energy
lower than 25 eV, the discharge voltage should be less than 45 V. The discharge current was fixed at 7.5 Amp, and the ion beam current is about 1.8 Amp (25% of discharge current). The processing pressure was based on the total Ar flow rate (no active control) and typically varied from 7 to 1.2 mTorr.

A residual gas analyzer (RGA) is installed on the top of processing pressure to monitor and control a reactive gases partial pressure during deposition. The reactive gas could be either maintained at certain partial pressure from RGA feedback controller or at certain flow rates by gas flow controller. The oxygen partial pressure varied from 5E-7 to 6E-6 Torr and the oxygen was introduced into the chamber either near the ion source or near the target position 1.

As shown in Figure 2-7, a shield was used to prevent cross-contamination among targets during co-sputtering. The picture of this system was taken facing the end-hall ion source. The 4-inch substrate holder and load lock are not shown. As discussed previously, the deposited films deposition rate and stoichiometry is not only controlled by reactive gas, but also by pulse frequency and applied potential. Because of the off-axis design, the low energy ion beam secondarily conditions the deposited films if a physical block is not put on the shielding to prevent direct line of sight between the ion source and the substrate.

![Figure 2-7. Schematic and picture of the 4Wave LANS chamber.](image)
2.3 Rapid thermal annealing (RTA)

A series of annealing experiments were done to assess the deposited oxide thin film thermal stability of resistivity and TCR. As shown in Figure 2-8, a homemade rapid thermal annealing system was used to post-anneal the deposited oxide thin films. The ambient gas (99.99% Ar or O₂ gas) was fed into the tube furnace at the flow rate of 2 L/min. The furnace was first preheated to 350°C. The samples were placed on a graphite boat and inserted into the tube for 20 min annealing. After annealing, the samples were moved to the end of the tube and cooled to room temperature in an Ar ambient.

Figure 2-8. Picture of homemade RTA used for annealing experiments.
2.4 Grazing incidence X-ray diffraction (GIXRD)

Grazing incidence x-ray diffraction utilizes the technique of x-ray diffraction with a small incident angle to increase the probability of evaluating a thin film’s crystallinity. In this work, the incident beam angle was fixed at 1° and the detector angle was scanned so that the 2θ angles varied from 5° to 70°. This geometry reduces diffraction signal from the substrate and limits the penetration depth of X-rays to be about 100 Å.

As shown in Figure 2.9, in this work, a PANalytic Pro X’Pert MPD with Cu Kα1 (λ=1.54 Å) radiation was used to collect the x-ray diffraction pattern. The collected data was analyzed by using the MDI JADE 9 software.

Figure 2-9. Picture of the GIXRD instrument used in this work.
2.5 Raman spectroscopy

Raman spectroscopy is a vibrational spectroscopy technique used to analyze chemical composition and structure of the materials. This technique is based on the frequency shifting of a monochromatic light caused by inelastic scattering by the sample. Raman spectra provide a spectral fingerprint of each molecule and can be analyzed both qualitatively and quantitatively.

In this work, the Raman spectra of a vanadium target and vanadium oxide thin films were collected using a Renishaw inVia Raman Microscope (Renishaw Inc., Gloucestershire, UK) with backscattering geometry. A HeNe (632.5 nm) laser was used as excitation source with a power around 5 mW, and a 100x microscope objective lens with a numerical aperture of 0.9 was used to collect the data. Since a silicon wafer was used as substrate, reference spectrum of Si was collected and subtracted from all the spectra.

2.6 Energy-dispersive X-ray spectroscopy (EDS)

Energy dispersive x-ray spectroscopy is a technique used to analyze and identify the elements in a sample. EDS utilizes the x-ray spectrum emitted by a sample surface bombarded by a high-energy focused electron beam. The incident electron beam excites an electron from an inner shell to an outer shell of an atom, and another electron from a higher energy shell fills the hole and release an x-ray. The number and energy of the x-ray photons are measured for both qualitative and quantitative analysis. Elements with atomic number from 4 to 92 can be detected.

In this work, the elemental analysis of metal oxide thin films was made by EDS spectroscopy using a field emission scanning electron microscope (NanoSEM 630). The collected data was analyzed by AZtecEnergy EDS analysis software (Oxford Instruments). Due to the statistical and analytical errors, the analytical accuracy is estimated about ± 5% (at%).
2.7 Surface profilometry

The deposited film thickness was measured by a Tencor Alpha-step 500 surface profilometer. The step was created by a Kapton tape or colloidal graphite at the center of wafer. After the film deposition, Kapton tape or the colloidal graphite was carefully removed by acetone. The height of the resulted step was measured using 50 µm to 2 mm scan lengths across the step. The reported thickness was typically an average by repeated measurements for different spots as well as different scanning direction. In addition to profilometry, the deposited metal oxide thin film thickness was also estimated from spectroscopic ellipsometry. The measured film thickness has a typical error $< \pm 2\%$.

2.8 Spectroscopic ellipsometry (SE)

As a non-destructive optical characterization method, spectroscopic ellipsometry is not only used to measure the thickness of thin films, but also provides optical information of a sample. The polarization of the incident light beam changes after interacting with a sample, and the change of the amplitude ratio $\Psi$ and the phase difference $\Delta$ are measured and quantified by further modeling. The sample thickness and optical properties can be extracted from the model.

In this work, a J.A. Woollam Co. RC2 multichannel spectroscopic ellipsometry with dual-rotating compensator was used to attain ex-situ and real time in-situ data. For ex-situ measurement, the light incidence angle was varied from 50° to 80° with a step of 10°. A Xe lamp and a Quartz Tungsten Halogen lamp installed in the RC2 instrument enable large spectral range from 0.73 to 5.15 eV (1700-240 nm). Figure 2-10 shows the photographs of RC2 instrument for ex-situ measurement.
The collected data of the deposited films were fitted to a model that contains a four-layer structure as shown in Figure 2-11. The Bruggman effective medium approximation (EMA) was used to calculate surface roughness as a mixture of 50% top bulk metal oxide layer and 50% voids.

Figure 2-10. Picture of J.A. Woollam RC2 SE instrument for ex situ measurement on the variable angle base.

Figure 2-11. Cartoon of the model structure with four layers.
2.9 Electrical properties characterization

Resistivity and temperature coefficient of resistance (TCR) of deposited thin films were measured by two methods. A four-point probe instrument was used to measure films sheet resistant and TCR mapping (usually 49 points for a 6 inch wafer) if the films sheet resistance below 800k Ω/square. Transmission line measurements of film resistivity were also conducted using 100-nm-thick Ti contacts sputtered through a stencil mask onto the deposited thin film surface.

The resistance $R$ between two Ti electrodes was calculated by I-V measurement with voltage from -5 to 5 V. The room temperature resistivity $\rho$ was calculated by:

$$ R = \frac{R_{sh}d_i}{w} + 2\frac{R_c}{w} \quad \text{Eq. 2.2} $$

$$ R_{sh} = w \times \text{slope} \quad \text{Eq. 2.3} $$

$$ \rho = t \times R_{sh} \quad \text{Eq. 2.4} $$

where $R_{sh}$ is the sheet resistance of thin film, $R_c$ is the contact resistance between the thin film and the contact, $d_i$ is the spacing between electrodes, $w$ is electrodes length, and $t$ is the thin film thickness. Figure 2-12 shows the TLM pattern and fitting graph to calculate film resistivity and contact resistance.

The resistance $R$ was measured on a two-point micro-probe station at temperatures ranging from 20-80°C with a step of 2°C, and the room temperature TCR values were calculated using the Eq 1-1 and 1-2. The calculated TCR values typically have an error of ±10%.
Photolithography

Photolithography is a process of transferring patterns on a mask to a thin film. In this work, the smallest features were $1\mu m \times 1\mu m$ and contact photolithography with 365 nm (i-line)
ultraviolet light source (LED array) was used to make patterns. Figure 2.14 shows the picture of the contact mask aligner used in this work (Karl Suss MA56 aligner).

Figure 2-13. A picture of Karl Suss M56 mask aligner.

Photolithography recipe varies for different oxide thin films and device structures. Wet etching was first tried to pattern NiOₓ film. Different etchants such as ammonium hydroxide, nitric acid, and sulfuric acid (at 60°C) have been tried to pattern NiOₓ thin films, and they did not etch NiOₓ films. CAN (ceric ammonium nitrate) at different temperatures also have been tried. The etch rate of NiOₓ by high concentration of CAN (1:1) is very slow at room temperature (1nm/min), whereas at 60°C the etch rate increases to about 1nm/sec. However, high concentration CAN at 60°C also etches the protecting photoresist (1811) very fast. Thus, in this work, NiOₓ active layers were patterned by a lift-off process. The processing recipe steps are
listed in Appendix A. Figure 2-14 shows the comparison between etching and lift-off patterning of NiO\textsubscript{x} thin films. The photolithography masks were designed by Myung-Yoon Lee, a graduate student in Jackson Electronics Research Group at The Pennsylvania State University.

Figure 2-14. NiO\textsubscript{x} active layer patterned by (a) CAN etching at 60\textdegree C for 3 min and (b) double-layer lift off process.

2.11 1/f noise measurement

As mentioned in Chapter 1, unlike the Johnson noise, the 1/f noise is dependent on material properties and processing parameters rather than just the film resistance. The low frequency 1/f noise for microbolometer sensing materials was extracted by using Hooge-Vandamme relation [69]:

$$\log\left(\frac{S_i(f)}{I_{bias}}\right) = \log\frac{\alpha_H}{n\times V} - \beta \log(f)$$

Eq.2-5

where $I_{bias}$ is the measured sample current, $S_i(f)$ is the spectral current density and $f$ is the frequency. $\frac{S_i(f)}{I_{bias}^2}$ is the power spectra density (PSD). $\alpha_H$ is the Hooge's parameter, $n$ is the carrier concentration, $V$ is the measured thin film sample volume, and $\beta$ is the slope of measured 1/f noise. It is hard to independently measure the VO\textsubscript{x} [46] and NiO\textsubscript{x} carrier concentration. In
order to compare 1/f noise among different materials, a normalized Hooge's parameter $\frac{\alpha_H}{n}$ is used as the property of interest.

![Diagram](image)

Figure 2-15. (a) and (b) Top and cross-section view of noise patterns; (c) volume dependence of PSD; and (d) Plot of log (PSD) versus log (frequency) to extract normalized Hooge’s parameter $\frac{\alpha_H}{n}$.

As shown in Figure 2-15, the 1/f noise of different volumes of a patterned NiO$_x$ film were measured, and the normalized PSD data is inversely proportional to the sample volume, which correlates to Eq. 2-5. The normalized Hooge’s parameter can be extracted by a linear fit to PSD versus frequency, in a log-log scale. The slope of the fitted line is about -1, again, confirming 1/f noise is measured. The intercept of this linear fit on Y-axis is used to extract the normalized Hooge’s parameter. The NiO$_x$ noise shown in this work was measured and analyzed by Myung-Yoon Lee.
Chapter 3
Reactive Magnetron Pulsed-dc Sputtering of Vanadium Oxide

As mentioned in the introduction, VOₓ thin films deposited by reactive magneton pulsed-dc sputtering with RF substrate bias have increased film density, improved TCR, and reduced 1/f noise when compared with those that do not use substrate bias. However, reactive magnetron sputtering is a complex process and the inherent non-uniform sputtering of the target as well as the specifics of the system being used must be taken into consideration. In this chapter, the potential of reactive pulsed-dc magnetron sputtering as an alternative to reactive ion beam sputtering to prepare VOₓ microbolometer thin films is investigated. Different processing parameters such as processing pressure, total gas flow rates, target to substrate throw distance, and gas delivery effects on process control and film uniformity are analyzed. We also report on other methods also have been tried in a "quick-and-dirty" way to find out if they might be useful to the microbolomometer industry to improve process controllability and overall yield. These processing methods include co-sputtering of V and V₂O₅ targets, reactive sputtering from a VC target, V₂O₅ target, V₂Oₓ target, and H₂ introduced into chamber plasma during deposition.

3.1 VOₓ thin films prepared by sputtering of metallic V target

3.1.1 The effects of processing pressure

VOₓ thin films were deposited with -240 V (25 W rf) substrate bias at 1, 5, and 10 mTorr pressure and with O₂/Ar inlet ratios of 0.08, 0.1, and 0.12. The oxygen inlet position was near the substrate and the throw distance was 8 inches. As shown in Figure 3-1 (a), for low O₂/Ar inlet ratios, the VOₓ deposition rate is higher at higher processing pressure. As the O₂/Ar inlet ratio
increases, the deposition rate of VO$_x$ decreases, and the decrease is greater at higher processing pressure. The deposited film resistivity and TCR values are shown in Figure 3-1(b). Resistivity and TCR increase with O$_2$/Ar inlet ratio increase and the resistivity change is greater at higher processing pressure.

Figure 3-1. VO$_x$ films deposited at different pressures as a function of O$_2$ to Ar inlet ratio with -240V substrate bias at an 8 inch throw distance with oxygen inlet position near the substrate. (a)VO$_x$ film deposition rate and (b) resistivity and TCR values.
Figure 3-2. Hysteresis curves of vanadium target cathode current versus O₂ to Ar inlet ratio, for 300 W pulsed DC, -240 V substrate bias, a total gas flow rate of 18 SCCM, throw distance of 8 inches, with oxygen inlet position near the substrate, and total pressures of 1, 5, and 10 mTorr.

To understand VOₓ thin film property changes with increasing of O₂ /Ar inlet ratio, the vanadium metal target oxidation was assessed by monitoring the target cathode current. As shown in Figure 3-2, the dependence of the cathode current with varying O₂/Ar inlet ratio is hysteretic. The dependence can be divided into three regions: a metallic zone at low O₂/Ar inlet ratio, where the target is initially oxidized and the cathode current is large; an oxidized zone at high O₂/Ar inlet ratio, where the target surface is oxidized and the cathode current is low, and; an intermediate zone, where the target surface is transitioning from metallic to oxidized and the cathode current is larger than for the oxidized target surface, but smaller than for the initially oxidized surface. The target hysteretic characteristic was observed before [62].
During reactive sputtering, the O\textsubscript{2} gas has, in general, three possible outcomes: some is consumed by the target surface, some is consumed by reaction with vanadium at the substrate and chamber walls, and some is pumped out of the vacuum chamber \cite{60}. In the metallic zone, the available oxygen is insufficient to significantly oxidize the V target and the measured cathode current is approximately the same as with no O\textsubscript{2} input. Ions are drawn from the magnetron plasma, the cathode current is approximately constant during the entire negative pulse time, and the sputter deposition rate is high. In the oxidized zone, the available oxygen is sufficient to fully oxidize the vanadium target surface. Because the conductivity of the surface VO\textsubscript{x} is low, the Ar/O\textsubscript{2} ion flux charges the target surface, the cathode current decreases rapidly during the target negative pulse time, and the deposition rate is reduced compared to the metallic target. The strength of the metal-oxide bonds for the oxidized target surface may also reduce the sputter yield, further reducing the deposition rate \cite{61}. Between the metallic zone and oxidized zone is an intermediate zone, where the V target is partially oxidized \cite{62} As shown in Figure 3-2, the intermediate zone occurs for O\textsubscript{2}/Ar inlet ratio from 0.07 to 0.2 at 1 mTorr, 0.06 to 0.12 at 5 mTorr, and 0.04 to 0.1 at 10 mTorr. A comparison of Figures 3-1 and 3-2 shows that films with the resistivity required for microbolometer use are deposited with the cathode current in or near the intermediate zone, where the target surface is transitioning from metallic to oxidized. At higher deposition pressure (5 and 10 mTorr), the transition from metallic to oxidized target surface is abrupt and control is difficult. Reducing the deposition pressure to 1 mTorr leads to a more gradual change from metallic to oxidized target surface and allows better control of deposited film properties. The results indicate that lower pressure (1 mTorr) is useful for reproducible deposition of VO\textsubscript{x} films in the 0.1 to 10 \(\Omega\text{•cm}\) resistivity range.
3.1.2 The effects of total gas flow rate

If the pumping speed is fixed by the adjusting the throttle valve, the processing pressure changes as a function of total gas flow rate. As shown in Figure 3-3, the hysteresis curves of the V target among different total gas flow rates are compared. The higher of the pressure and total gas flow rate, the higher of the cathode current. This may be due to more Ar$^+$ bombarding to the target. Higher total gas flow rate means at the same O$_2$/Ar inlet ratio, the oxygen flow rate is higher, which may lead to the faster oxidization of the target. On the other hand, higher total gas flow rate recovers the oxidized target faster. This may explain the hysteresis curve is slimmer when total gas flow rate is higher. Though the higher pressure indicates higher deposition rate, the fast transition between metallic zone to oxidized zone leads to poor process controllability.

Figure 3-3. Vanadium target hysteresis curve comparison with different total gas flow rate. The pumping speed is fixed. Throw distance is 8 inch. The oxygen inlet position is near substrate and pulsed dc power applied on target is 300 W. Substrate bias voltage is -240 V.
3.1.3 Gas delivery and throw distance effects

The effects of target to substrate throw distance and oxygen inlet position were also investigated. During deposition, the pulsed dc power was fixed at 300 W and the processing pressure was 5 mTorr with a total gas flow rate of 18 SCCM. The film deposition time was 900 seconds and the substrate was rotated at 20 rpm. The substrate bias was fixed at -240 V and the throw distance was changed by moving the V target position.

![Graph showing cathode current vs. oxygen to Ar ratio for different throw distances](image)

Figure 3-4. Vanadium target hysteresis curve comparison for different throw distances. Total gas flow rate of 18 SCCM. Throw distance varies from 1 inch, 4 inch, to 8 inch. The oxygen inlet position is near substrate. Processing pressure is 5 mTorr and pulsed dc power applied on target is 300 W. Substrate bias voltage is -240 V.

Figure 3-4 shows the hysteresis curves with different throw distances. Target hysteresis curve has wider window when throw distance is shorter. This indicates that the throw distance has influences on the conditioning of target. When throw distance is 1 inch, the intermediate zone is when O₂/Ar inlet ratio is between 0.05 and 0.15. With increasing of the throw distance, this
intermediate zone width changes to between 0.08 and 0.14 when throw distance is 4 inch, and 0.07 to 0.12 when throw distance is 8 inch. At the metallic zone, the higher throw distance has higher cathode current.

In the CMS-18 deposition system, the target shutter was closed for pre-conditioning of the target. However, the target condition changes once the target shutter is opened for film deposition. This leads to the composition of the initial layer of deposited film being less controllable and more variable. Thus, a substrate shutter rather than the target shutter should be used to improve the controllability of the sputtering process.

Figure 3-5. VO₃ thin films deposition rate for two different oxygen inlet positions at different target to substrate throw distances (4 inch or 8 inch), with the oxygen inlet either near the substrate or near the target.
Figure 3-6. VO\textsubscript{x} thin film resistivity and TCR for two different oxygen inlet positions at different target to substrate throw distances (4 inch or 8 inch), with oxygen inlet either near substrate or near target. The yellow region shows the resistivity range of interest from 0.1 Ω•cm to 10 Ω•cm.

Figures 3-5 and 3-6 show the VO\textsubscript{x} thin film deposition rate, resistivity and TCR values for VO\textsubscript{x} thin films prepared at different throw distances and oxygen inlet positions. As shown in Figure 3-5, at a fixed throw distance (either 4 inch or 8 inch), before the V target is fully oxidized (O\textsubscript{2}/Ar inlet ratio <0.12), the deposition rate, resistivity and TCR values of VO\textsubscript{x} films are higher when the oxygen inlet is near the substrate. Introducing oxygen near the substrate tends to favor greater oxidation at the substrate thus increasing film resistivity, while keeping the target surface more metallic than for the same O\textsubscript{2} ratio near the target. At high O\textsubscript{2}/Ar inlet ratio (>0.12), the target is in the oxidized zone and the deposition rate and the VO\textsubscript{x} film resistivity are similar for oxygen introduced near the target or near the substrate.
Figure 3-5 shows that at the lowest O$_2$/Ar inlet ratio, the target is in the metallic zone, and the film deposition rate is a strong function of throw distance, with larger throw distance leading to lower deposition rate. This is primarily a geometric effect, but there is also a target surface composition component. Introducing oxygen near the target leads to greater target oxidation and lower sputtering rate, so for both 4” and 8” throw distance the deposition rate is lower for oxygen introduction near the target.

As the O$_2$/Ar inlet ratio increases the film deposition rate first increases then decreases. The film deposition rate is a function of both the target surface oxidation and additional vanadium oxidation either in the sputtering ambient or at the substrate surface. To first order, the sputtering rate correlates with the target cathode current. From the target hysteresis curve (Figure 3-4), the sputtering rate should decrease with increasing O$_2$/Ar ratio. The increasing deposition rate shown in Figure 3-5 results from increasing oxidation of the depositing vanadium, that is, the film composition is changing as more oxygen is incorporated. Figure 3-6 shows that film resistivity increases greatly (> 3 orders of magnitude) as the O$_2$/Ar inlet ratio increases from 0.05 to 0.15, consistent with more fully oxidized vanadium. For 8” throw distance, with increasing O$_2$/Ar inlet ratio the increase in film thickness that results from increasing oxidation approximately counters the decreasing sputter rate and the deposition rate changes relatively little. For 4” throw distance, the increased target surface oxidation from the substrate bias plasma leads to a decreased sputtering rate that dominates, and for O$_2$/Ar inlet ratio greater than 0.12 the deposition rate is lower than for the larger throw distance.

The results show that when the vanadium metal target is not fully oxidized (in the metallic zone and intermediate zone), both throw distance and oxygen inlet position play important roles in the deposition rate and electrical characteristics of pulsed dc sputtered VO$_x$ thin films. This provides a tool to deposit VO$_x$ films in the desired resistivity range. By using a long throw distance and introducing oxygen near the substrate, it is possible to increase the sputter
ambient and substrate vanadium oxidation to increase the deposited film resistivity to the desired range while maintaining the vanadium sputtering target surface in the stable metallic zone.

### 3.1.4 The analysis of non-uniform oxidization of V target

As discussed in Chapter 2, during reactive magnetron sputtering, the plasma density is non-uniform across the target surface, and the discharge current density is higher in the racetrack region formed by the target magnetic field. For non-reactive sputtering, this leads to a sputtering rate that varies widely across the target surface and results in a racetrack erosion pattern for well-used targets. For reactive sputtering, the varying plasma density and sputtering rate can also lead to variations in the target surface composition [60], [63]. For example, for a constant O₂/Ar inlet ratio in the metallic or intermediate zone, higher sputtering rate leads to less target surface oxidation because the available oxygen is not sufficient to oxidize the rapidly eroding target surface. Where the sputtering rate is lower the target surface will be relatively more oxidized. As described earlier, the oxidized target surface leads to a further reduction in sputtering rate. Thus, for reactive magnetron sputtering the target surface composition is expected to be non-uniform.

Figure 3-7 shows the top-view picture and cross-section schematic of a well-used vanadium target. The racetrack region (valley) has higher consumption compared to other regions (hills). After being sputtered with 300 W of power for 15 minutes and an O₂/Ar inlet ratio equal to 0.15, the non-uniform oxidization across the vanadium target was analyzed by Raman spectroscopy in order to evaluate the stoichiometry at different spots on the target.
Figure 3-7. Top view and cross-section of V target. The cross-section shows positions analyzed by Raman spectroscopy.

As shown in Figure 3-8, points 1, 4 and 8 have similar Raman features. The low frequency peaks at 275 cm\(^{-1}\) suggest the existence of defective FCC nanocrystalline domains as found in previous studies correlating TEM and Raman results for numerous VO\(_x\) films [33], [36], [41]. The high frequency feature of points 4 and 8 at around 930 cm\(^{-1}\) suggest the existence of V\(^{5+}\)=O consistent with polycrystalline V\(_2\)O\(_5\) V\(^{5+}\)=O stretching peak. The high frequency peak of point 1 shifts to 890 cm\(^{-1}\) which suggest the existence of V\(^{4+}\) double bonded to oxygen[35][70]. These target surface areas are strongly oxidized. Points 3 and 5 only show peaks at 275 cm\(^{-1}\)are somewhat less oxidized. Points 2, 6, and 7 show no obvious Raman VO\(_x\) features, indicating that these target surface areas are metallic.
Figure 3-8. Raman spectroscopy analysis of different positions across the V target. Measured positions are shown in Figure 3-7.

Figure 3-9. Picture of non-rotated substrate mounted on the target shutter with 1-in throw distance.
To study the V target non-uniform sputtering and composition effects on the deposited VO$_x$ thin films, non-rotated and rotated films were prepared at different throw distances at 5 mTorr. As shown in Figure 3-9, non-rotated substrate was mounted on the target shutter to collect data for 1-inch throw distance. For the 1-inch throw distance the oxygen was introduced in near the target with O$_2$/Ar inlet ratio equal to 0.15. As shown in Figure 3-10, the resistivity of the deposited film is lower at the center and higher at the edges. This is expected, because in this close spaced sputtering configuration, gas that reaches the target center must pass through the edge region. In doing so much of the oxygen is consumed and the oxygen-depleted Ar that reaches the target center results a lower resistivity for the sputtered VO$_x$ thin film. The non-rotated and rotated films at 4-inch and 8-inch throw distance were deposited with an O$_2$/Ar inlet ratio equal to 0.1 on 6 inch wafers with oxygen inlet near the substrate. The resistivity of a non-rotated VO$_x$ film varied from 0.02 to 0.2 Ω•cm at a 4-inch throw distance, and from 0.4 to 0.8 Ω•cm at an 8-inch throw distance. The deposited films’ uniformity can be further improved by rotating the substrate during deposition. At a 4-inch throw distance, the rotated film resistivity varied from 0.017 to 0.07 Ω•cm, whereas at an 8-inch throw distance film resistivity varied from 0.6 to 0.86 Ω•cm. The resistivity mapping of non-rotated and rotated samples at different throw distance are shown in Figure 3-11. This suggests the longer throw distance allows target non-uniformities to be averaged and results in improved uniformity of deposited films.

Figure 3-12 shows the TCR of VO$_x$ films deposited by reactive pulsed-dc magnetron sputtering is comparable to films deposited by ion beam deposition. The results demonstrate that by optimizing process parameters, reactive pulsed-dc magnetron sputtering can be an industrial alternative for depositing VO$_x$ films for microbolometers.
At 1 inch throw distance, VO$_x$ deposited on 4 inch non-rotated substrate at O$_2$/Ar=0.15.

At 4 and 8 inch throw distances, VO$_x$ deposited on non-rotated and rotated 6 inch wafers at O$_2$/Ar=0.1.
Figure 3-11. Resistivity mapping of VO$_x$ films when oxygen inlet position near substrate at a (a) 4 inch throw distance non-rotated (b) 8 inch throw distance non-rotated (c) 4 inch throw distance rotated and (d) 8 inch throw distance rotated. The oxygen to Ar inlet ratio is 0.1 and substrate bias is -240V.
3.2 VOₓ thin films deposited by co-sputtering of V and V₂O₅ targets

The target hysteresis, non-uniform oxidization of metallic target surface, oxygen delivery effects, throw distance, and processing pressure all influence the controllability of the sputtering process. Previous work has shown that the process window is very narrow for depositing VOₓ thin films of a specific composition by using one metallic V target in the magnetron pulsed dc reactive sputtering process. Will the co-sputtering of metallic target and oxide target improve the controllability and repeatability of the process? With low oxygen flow rate, the V target is sputtering low resistivity FCC VOₓ constituent and the V₂O₅ target is sputtering high resistivity amorphous V₂O₅ constituent. In this section, the VOₓ were deposited from metallic V and V₂O₅.
targets by co-sputtering, and different processing parameters such as substrate bias and oxygen flow rates were varied.

In this set of experiments, the V target was pulsed dc biased by 300 W and V₂O₅ was applied with 200 W of rf power. The processing pressure was fixed 5 mTorr and total gas flow rate was 18 SCCM. The throw distance was 8 inch and oxygen inlet was introduced through a gas ring 1 inch below substrate.

The deposited films resistivity and TCR values were mapped with and without substrate bias. The oxygen to Ar ratio is 0.05 and the V target was in the metallic regime. Figure 3-13 (a) and (b) show that without substrate bias, the deposited film resistivity varying from 2.25-1.72 Ω·cm whereas TCR from negative 2.92-2.36 %/K from wafer center to perimeter. This phenomenon corresponds to Gauntt’s [39] observation of a VOₓ sample deposited by one V target in reactive environment without substrate bias when rotation speed is 10 rpm. Because rO₂ is 0.05 and V target is at the metallic regime, the sputtering rate of V target is larger than V₂O₅ target. The deposited film is mainly determined by the sputtered V species reacting with O₂ on substrate. The decreasing of resistivity from center to edge is presumed to be due to the different time for reaction to occur on the substrate [39]. As is the usual trend, the TCR is decreasing when film resistivity decreases.

Figure 3-13 (c) and (d) show the deposited films with substrate bias and all the other processing conditions are the same. From the wafer center to perimeter, the resistivity varies from 0.21-0.42 Ω·cm. This opposite behavior suggests that the rf self-bias on substrate is affecting the substrate during the deposition. With substrate bias, the lower resistivity VOₓ region shows higher TCR values, indicating the change of microstructure of VOₓ and enhanced electrical properties.

Although using dual targets for co-sputtering has the potential to improve the repeatability of process by controlling the V target in metallic regime, the resistivity and TCR
mapping indicates that the deposited film on a 6-inch wafer is not uniform, even when the substrate is rotated at 10 rpm. Will the uniformity across the wafer be improved by increasing of oxygen to Ar ratio? As shown in Figure 3-14, when the rO₂ increases to 0.075, the film deposition rate increases to 1.8 Å/sec, which is 35% higher than that for a film sputtered from single V target under the same processing parameters. However, when rO₂ further increases to 0.1, the film deposition rate decreases indicating the beginning of oxidization of the V target. In order to prevent the V target from being oxidized and keep the higher deposition rate, rO₂ should not be greater than 0.1. When the rO₂ is fixed at 0.075, the VOₓ film deposited by co-sputtering resistivity and TCR values are mapped. By comparing Figure 3-15 (a) and (b) to Figure 3-13 (c) and (d), the VOₓ deposited with rO₂ = 0.075 shows better uniformity compared to the one deposited rO₂= 0.05. Figure 3-11 shows the resistivity versus TCR values of VOₓ thin films deposited by co-sputtering of V and V₂O₅ targets under different conditions, showing comparable properties with VOₓ prepared by Wood using IBD [3].
Figure 3-13.6 inch wafer mapping of VO$_x$ deposited by co-sputtering of V and V$_2$O$_5$ targets, rO$_2$ is 0.05 and substrate is rotated at 10 rpm: (a) resistivity and (b) TCR mapping without substrate bias; (c) resistivity and (d) TCR mapping with 25 W substrate bias. Resistivity unit is Ω•cm and TCR unit is -%/K.
Figure 3-14. The VO$_x$ films deposition rates (measured at the center of 6” wafer) change as a function of rO$_2$, deposited by V and V$_2$O$_5$ co-sputtering.

Figure 3-15. VO$_x$ films (a) resistivity and (b) TCR mapping deposited by V and V$_2$O$_5$ co-sputtering when rO$_2$ is 0.075.

Figure 3-16. TCR vs. Resistivity of VO$_x$ films deposited by co-sputtering of V and V$_2$O$_5$ targets show comparable properties with VO$_x$ prepared by Wood IBD method [3].
3.3 VO\textsubscript{x} thin films deposited using a vanadium carbide (VC) target

In addition to co-sputtering from metallic V and V\textsubscript{2}O\textsubscript{5} target, different targets such as vanadium carbide (VC), and vanadium oxide (V\textsubscript{2}O\textsubscript{x}) were also investigated to sputter VO\textsubscript{x} thin films for infrared imaging. In the first section, VO\textsubscript{x} thin films were sputter deposited from a vanadium carbide (VC) target on 100nm thermal oxide substrates. All the films were deposited for 900 sec and the VC target was pulsed dc biased with 300 W of power. The substrate was rf biased by -240 V (25W). The total gas flow rate was fixed at 18 SCCM whereas the processing pressure was 5 mTorr.

As shown in Figure 3-17, similar to metallic V target, the VC target shows hysteresis behavior by varying the oxygen to Ar inlet ratio. Even though the power applied on the target remained the same, the cathode current of the VC target current was lower than the pure V target due to lower conductivity (about half of pure V target) [71], indicative of lower deposition rate. Table 3.1 shows the deposition rate, resistivity, and TCR values of VO\textsubscript{x} deposited from the VC target with oxygen to Ar ratio varied from 0.05 to 0.2. Though the cathode current and deposition rate change gradually, the deposited VO\textsubscript{x} resistivity increases abruptly from metallic to high resistive. The poor process control and low deposition rate suggest that reactive sputtering from a VC target may not be a good option to deposit VO\textsubscript{x} for microbolometers.
Figure 3-17. Hysteresis loop of the VC target monitored by cathode current

Table 3-1. Deposition rate, resistivity, and TCR values of VO$_x$ sputtered from a VC target

<table>
<thead>
<tr>
<th>O$_2$/Ar ratio</th>
<th>Deposition Rate (Å/sec)</th>
<th>Resistivity (Ω•cm)</th>
<th>TCR (%/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.8</td>
<td>9.13E-4</td>
<td>+0.18</td>
</tr>
<tr>
<td>0.1</td>
<td>0.7</td>
<td>8.9E4</td>
<td>-0.35</td>
</tr>
<tr>
<td>0.2</td>
<td>0.7</td>
<td>2.9E4</td>
<td>-4.01</td>
</tr>
</tbody>
</table>
3.4 VOₓ thin films deposited from a V₂O₅ target or a V₂O₆ target

Previous study shows that increasing the substrate bias on VOₓ thin films (reactive sputtered from a V target) increases film internal strain by nanotwin formation; and the resistivity, TCR and film growth rate keep decreasing with increasing substrate bias [46]. In order to avoid the process complexity introduced by reactive sputtering, in this section, the substrate bias effects on VOₓ thin films sputtered from a V₂O₅ target and a V₂O₆ target without additional O₂ is discussed. Four samples were deposited from a V₂O₅ target applied with 300 W RF power at different substrate bias. Total Ar gas flow rate was at 18 SCCM and processing pressure was 5 mTorr.

Figure 3-18 shows the deposition rate, resistivity, and TCR decrease with an increasing of substrate bias. The deposition rate of VOₓ by a V₂O₅ target with 25 W substrate bias is about 1/3 of the rate when using a V target under the same conditions. Figure 3-13 also shows that the film with resistivity at 0.1 Ω·cm only has a TCR of -0.4 %/K, which is much lower than its counterpart (-2.5 %/K) deposited by reactive sputtering of a metallic V target. The low deposition rate and poor bolometric properties of these samples suggest it is not an optimal method for industrial fabrication.
Figure 3-18. VO₅ thin film thickness, resistivity and TCR values sputtered from the V₂O₅ target change as a function of substrate bias.

VOₓ thin films sputter deposited from a V₂O₅ target at different substrate bias were also studied. Before the films were deposited, the hysteresis behaviors of the V₂Oₓ target were assessed by monitoring the cathode current. The V₂O₅ target was pulsed-dc biased with 300 W power and oxygen to Ar ratio varied from 0 to 0.25. As shown in Figure 3-19, under three different processing pressures (1, 5, and 20 mTorr), the cathode current shows no obvious hysteresis behavior as a function of oxygen to Ar inlet ratio, indicative of good process control. However, the target current is lower than the metallic target under the same processing parameters, suggesting lower deposition rate. Though there is no hysteresis behavior of the V₂Oₓ target, similar to the metallic V target, the cathode current of the target change more gradual with increasing of oxygen to Ar ratio, indicating better control of deposited film composition and resistivity.
Figure 3-19. Hysteresis curve of V$_2$O$_x$ target under different processing pressures.

Figure 3-20 shows the VO$_x$ thin films deposited from the V$_2$O$_x$ target with different substrate bias. Similar to VO$_x$ deposited from the V$_2$O$_5$ target, the increasing of substrate bias during deposition decreases deposited films resistivity and TCR. The resistivity of the film deposited at 45 W substrate bias is 0.03 Ω•cm and the TCR is -1.3 %/K, which about half of the VO$_x$ is prepared with pure V target at the same resistivity. Even though the V$_2$O$_x$ target suggests possible good process controllability, the VO$_x$ thin film deposited from this target have lower deposition rate and limited TCR value compared to the one prepared from the metallic V target.

Figure 3-20. Resistivity and TCR values of VO$_x$ thin films sputter deposited from V$_2$O$_x$ target with different substrate biases.

3.5 VO$_x$ thin films reactive sputtered from a V target with oxygen and hydrogen

Previous study shows post-deposition H$^+$ implantation to deposited VO$_x$ thin films increase both film resistivity and TCR. [41] In this section, in order to study the hydrogen effects
on VO\textsubscript{x} thin films properties, two samples were prepared with and without hydrogen introduced into the plasma during deposition. Both of these VO\textsubscript{x} samples were reactive sputtered from the metallic V target with 300 W pulsed-dc power supply and -240 V substrate bias at 5 mTorr. The first sample was deposited in a mixture of Ar and O\textsubscript{2}, and the total flow rate was 18 SCCM and O\textsubscript{2}/Ar inlet ratio was 0.05. The second sample was deposited with the same processing parameters except H\textsubscript{2} was introduced into the chamber during deposition, and both H\textsubscript{2}/Ar and O\textsubscript{2}/Ar ratio was 0.05.

As shown in Figure 3-21, the resistivity versus TCRs of these two samples (different points measured across 6-in wafer) were plotted and compared to ion beam deposited sample. The graph shows that though the resistivity does not change much with introducing of H\textsubscript{2} during deposition, the TCR reduced about 20-25%, which is unsuitable for microbolometer usages. This result is quite different from the earlier report of H\textsuperscript{+} implantation.

![Figure 3-21. TCR versus resistivity of VO\textsubscript{x} thin films prepared by ion beam deposition and reactive pulsed-dc magnetron sputtering.](image)
3.6 Conclusion

In this Chapter, the potential for reactive pulsed-dc magnetron sputtering of nanocomposite VO$_x$ thin films for microbolometers was discussed. Processing pressure, throw distance, and the delivery of oxygen have large effects on the deposition rate and electrical properties of VO$_x$ films. To deposit uniform VO$_x$ with characteristics suitable for thermal images long throw distance and oxygen inlet position near the substrate are useful. Lower processing pressure leads to more gradual transition of target surface oxidization and better control of deposited film properties, but also results in lower deposition rate. Reactive co-sputtering of metallic V and V$_2$O$_5$ target increase the vanadium oxide thin film deposition rate and also improve film uniformity, which might be an alternative industrial method to prepare VO$_x$ microbolometer thin films.

Different methods were also investigated in a "quick-and-dirty" way improve processing controllability. However, the VO$_x$ prepared from a V$_2$O$_5$ target, V$_2$O$_x$ target, and VC target show lower deposition rate and limited bolometric properties compared to the ones reactive sputter deposited from a metallic V target. Introducing of hydrogen into chamber plasma during deposition reduces as-deposited VO$_x$ TCR values but not resistivity. These initial results did not provide any results that would indicate that they are more suitable for microbolometer industry to fabricate VO$_x$ thin films than the reactive sputtering of a vanadium target with Ar and oxygen.
Chapter 4

High Resistivity and High TCR VO<sub>x</sub> Thin Films Prepared by Biased Target Ion Beam Deposition

In this chapter, VO<sub>x</sub> thin films were prepared by the biased target ion beam deposition system (BTIBD) mentioned in Chapter 2. Unlike magnetron sputtering, this system utilizes uniform sputtering of targets implying a more uniform stoichiometry of sputtered species. As mentioned in Chapter 2, a lower energy plasma (<25 eV) is remotely generated by an end-Hall ion source, the three targets are independently biased by three pulsing units, and the oxygen partial pressure is controlled by a residual gas analyzer installed on the top of processing chamber. The independent controllability of the ion source, target, and reactive gas of the BTIBD system provides flexibility in the processing parameters that can be used to engineer deposited film properties. In this work, the deposited film deposition rates and electrical properties are varied by controlling the oxygen partial pressure, oxygen inlet position, source Ar flow rates, target pulse width, and target bias voltage. Results for VO<sub>x</sub> thin films doped with Mo are also investigated. VO<sub>x</sub> films deposited by BTIBD system show high TCR (<-4.5%/K), high resistivity (>1000 Ω•cm) and good thermal stability. These prepared high resistivity and high TCR VO<sub>x</sub> thin films are candidates as active sensing layers for vertical-structure pixels of microbolometers, which will be discussed in the last section of chapter.

4.1 The effects of oxygen partial pressure and oxygen inlet position

VO<sub>x</sub> thin films were prepared by the BTIBD system in a mixture of Ar and O<sub>2</sub> ambient. Three metallic V targets with 99.99% purity were pulsed-dc biased at -800 V with 10 kHz pulse repetition rate and 1μsec pulse width. The end-Hall ion source discharge current was set to be 7.5 Amp and discharge voltage was about 40 V. The oxygen partial pressure (ppO<sub>2</sub>) was monitored
and controlled by a residual gas analyzer and was varied from 5E-7 to 2.6E-6 Torr. The total chamber pressure was set by the Ar and O₂ flows (no active pressure control) and was approximately 0.74 mTorr. The ion source and hollow cathode Ar flow were 60 and 10 SCCM respectively. The trends for the as-deposited VOₓ thin films deposition rate, resistivity, and TCR as a function of oxygen partial pressure, and oxygen inlet position is discussed.

Figure 4-1 (a) and (b) show that when oxygen is introduced through the ion source, the cathode current for the three targets, the deposition rate, and the electrical properties of the deposited VOₓ change as a function of ppO₂. With increasing ppO₂, the cathode current decreases linearly, indicating continuous oxidation of all three targets. The film deposition rate is related to the target bias current. When the oxygen inlet position is near target position 1, a similar trend has been observed (Figure 4-1(c)). Though the target cathode current and film deposition rate decrease gradually with increasing the oxygen partial pressure, the film resistivity increases abruptly from 1E-3 to 1E3 Ω•cm with only a 1E-7 Torr increase of ppO₂. When oxygen is introduced through the ion source, the resistivity threshold is at an oxygen partial pressure of 6E-7 Torr, and 8E-7 Torr when oxygen is near target position 1. This may be because when the oxygen inlet is in the end-Hall source, the target is oxidized faster due to a higher oxygen species energy since oxygen is used as working gas with Ar. However, unlike magnetron reactive sputtering that was discussed in Chapter 3, the oxygen inlet position does not affect the as-deposited VOₓ properties significantly. Figure 4-1 shows that the as-deposited VOₓ films have resistivity in the range of 2E3 Ω•cm to 1E5 Ω•cm and TCR from -3.9 %/K to -5.2 %/K. The VOₓ films with resistivity lower than 1E-3 Ω•cm have TCR than -0.06 %/K, which is not of interest for microbolometer applications.
Figure 4-1. VOₓ thin films properties change as a function of oxygen partial pressure: a) and b) when oxygen inlet at end-hall; b) and c) oxygen inlet near target VOₓ thin films deposited with three V targets with substrate bias voltage -800 V and pulse width/pulse period 1 µsec/100 µsec. The HC flow rate is 10 SCCM whereas the ion source Ar flow rate is 60 SCCM. The discharge current is 7.5 Amp and discharge voltage is around 40 V. The numbers in red are the TCR values with unit of -%/K.
4.2 The effects of source Ar flow rate (processing pressure)

As mentioned in Chapter 2, the Ar+ ions generated by the ion source are about 60-70% of the ion source discharge voltage. Since in our BTIBD system the ion source discharge current is fixed to be 7.5 Amp, the discharge voltage is a function of source Ar flow rate: the higher the Ar flow rate the lower the discharge voltage. In this section, the effects of source Ar flow rate on deposited VO$_x$ thin film deposition rate and electrical properties are discussed. Similar to last section, three V targets were biased with -800 V with 10 kHz frequency and 1 μsec pulse width. Hollow cathode Ar flow was 10 SCCM, and source Ar flow rate was set to be 30 SCCM and 80 SCCM. Ion source discharge current was fixed at 7.5 Amp. The discharge current was 7.5 Amp and discharge voltage was around 70 V when source Ar was 30 SCCM and 35 V when source Ar was 80 SCCM. Oxygen was introduced near target position 1.

Figure 4-2 (a) shows that when the source Ar flow rate is 30 SCCM, with increasing ppO$_2$, the deposition rate first increases then decreases. The initial increase of the deposition rate suggests the three V targets have not fully oxidized yet, and the sputtered V species actively react with oxygen in the chamber plasma and near the substrate. Further increase of ppO$_2$ leads to oxidization of the three V targets and hence, decrease of film deposition rate. Again, the film resistivity increases abruptly from about 1E-3 to 2000 Ω•cm when ppO$_2$ increases from 1.2E-6 to 1.3E-6 Torr. Figure 4-2(b) shows that at high source Ar flow rate (80 SCCM), the film deposition rate decreases continuously with increasing ppO$_2$, and the resistivity again increases from 1E-3 to 1E3 Ω•cm when ppO$_2$ changes from 7E-7 to 8E-7 Torr. The result shows that the resistivity threshold increases to higher ppO$_2$ with an increase in the source Ar flow rate. This is probably due to higher Ar flow rate depletes the oxygen concentration near the V target surface at the same ppO$_2$. Thus higher ppO$_2$ is needed to fully oxidize the target surface.
4.3 The effects of target bias voltage

In order to investigate the effect of bias voltage on the composition and electrical properties of VO\textsubscript{x} films, the voltage of all three targets was varied from -300 V to -800 V. The oxygen inlet was fixed near Target 1, and the hollow cathode Ar flow rate was 10 SCCM while the source Ar was 60 SCCM.
Figure 4-3. VO\textsubscript{x} film deposition rate and resistivity change as a function of increasing target bias voltage.

Figure 4-3 shows when all three targets pulse width/pulse period is 1/100 µsec and ppO\textsubscript{2} remains at 8E-7 Torr, the deposition rate increases as a function of target bias voltage. The increase in deposition rate is likely due to higher bombardment energy of Ar\textsuperscript{+} which leads to a higher sputtering yield. When bias increases from -300 V to -700 V, the VO\textsubscript{x} films resistivity drops two orders of magnitude, indicating the increasing target bias voltage removes the oxide layer of oxidized targets more efficiently thereby allowing lower valence or more metallic V species arrive at the substrate surface. When target bias voltage increases form -700 V to -800 V, the deposited film resistivity dramatically drops from 1E3 Ω\textperiodcentered cm to 1E-3 Ω\textperiodcentered cm. This is corresponding to previous observation and indicates the strong threshold for sputtering of metal versus oxide, which is typical in reactive sputtering. For this ppO\textsubscript{2}, VO\textsubscript{x} films made with a bias between -300 and -700 V have a TCR higher than -4.5%/K are prepared with resistivity higher than 2E3 Ω\textperiodcentered cm.
4.4 The effects of pulse width on biased targets

Results from last few sections show that in this BTIBD system, even when adjusting ppO$_2$, oxygen inlet position, source Ar flow rates, and target bias voltage, it is hard to prepare VO$_x$ thin films in the resistivity range of 0.01-10 Ω•cm. In Chapter 3 we discussed that the co-sputtering deposited VO$_x$ films from the metallic V and V$_2$O$_5$ targets showed good bolometric properties in the resistivity range of 0.01 to 10 Ω•cm. This begs the question can the composition and properties of BTIBD prepared VO$_x$ thin films be controlled by using multi-target co-sputtering? By controlling the pulse width of three targets, the surface oxidized level of the target surface can be controlled. Thus, in this section, three V targets were biased at the same voltage but with a different pulse width individually. All the three targets were biased with -800 V at a 10 kHz frequency, and the pulse width was used to control the sputtered species from different targets. The oxygen was introduced near target position 1 and the ppO$_2$ was fixed at 8E-7 Torr. The source Ar and hollow cathode Ar were 60 and 10 SCCM respectively, and the processing pressure was about 0.74 mTorr. The source discharge current was fixed at 7.5 Amp and the discharge voltage was about 40 V. The pulse width of the three targets varied from 1 to 20 µsec, individually.
Figure 4-4. VO\textsubscript{x} thin films properties change as a function of pulse width applied on different targets: VO\textsubscript{x} deposition rate and resistivity change as a function of different pulse width of biased targets.

As shown in Figure 4-4, when all three targets are pulsed with a 1 µsec pulse width, the deposited VO\textsubscript{x} film is metallic (6E-4 Ω•cm). When all three targets are pulsed with a width of 20 µsec, the deposited film has high resistivity (1E4 Ω•cm). With increasing of the pulse width, the films resistivity increases. When one target is applied with a 10 µsec pulse and the two other targets are pulsed with a 1 µsec pulse, the deposited film is not uniform across the 4 inch wafer. The film resistivity was found to be about 0.01 Ω•cm at center, and 350 Ω•cm at the edge. This set of experiments did not produce films in the desired resistivity range.

Another set of experiments were done by varying target pulse width at higher processing pressure (1.74 mTorr). Because there was no active control of the processing pressure in this system, the flow rates of hollow cathode Ar and source Ar were increased to 100 SCCM each (highest value). In this set of experiments, the oxygen inlet position was moved back to the ion
source and the ppO₂ was fixed at 5E-7 Torr (before the targets were fully oxidized, refer to Figure 4-1 (a)). The target bias voltage was still -800 V with 10 kHz frequency. The ion source discharge current was 7.5 Amp and discharge voltage was about 35 V with 100 SCCM source Ar flow rate.

The three target pulse width varied from 1 to 15 µsec. When all three target pulse width is at 1 µsec, the deposited VOₓ film is uniform and has a resistivity of 5E-4 Ω•cm. When the three target pulse width is 5, 8, 10 µsec respectively, the deposited film is non-uniform, even with 20 rpm substrate rotation. As shown in Figure 4-5, at the center the film resistivity is ~3E-3 Ω•cm and at the edge is 8.7 Ω•cm. The film edge thickness is ~15% higher than the center. The result indicates that even a sample can be prepared in the resistivity range of 0.01-10 Ω•cm, the film has poor uniformity.

Figure 4-5. A non-uniform VOₓ film sample resistivity, TCR, and thickness varied from film center to edge.
Raman spectroscopy was used to study the structure of the non-uniform sample which is shown in Figure 4-5. From the sample center to edge, the resistivity is 0.03 Ω•cm, 3.2 Ω•cm, and 8.7 Ω•cm. From Figure 4-6 (a) we can tell with from the center to edge, the intensity of V-O-V bends at 295 cm$^{-1}$ decreases and V$^{5+}$=O double stretch intensity at 890 cm$^{-1}$ increases. The peak shows at 295 cm$^{-1}$ is observed to correlate to the FCC nanocrystalline domains, which decreases the film resistivity[35]. Figure 4-6(b) shows the Raman spectra of VO$_x$ prepared by ion beam deposition and magnetron pulsed dc sputtering with and without substrate bias. It shows that low resistivity VO$_x$ prepared by BTIBD has the similar features to the samples prepared by IBD and magnetron pulsed dc sputtering with substrate bias. The Raman spectrum of the high resistivity sample with resistivity of 5.9E3 Ω•cm only shows the strong peak of V$^{5+}$ double bond and moves to high frequency at about 920 cm$^{-1}$. From the non-uniform sample's Raman spectra, we believe that in the film center there is more FCC nanocrystalline domains than the edge. At this high pressure, the plasma is not as uniform, thus the formation of the nanocrystalline material may be due to a high-energy tail of source Ar+ ions bombarding the sample. This extra energetic argon may reduce the amount of oxygen that is bonded when compared to the edge.
The results from this set of experiments suggest that when using this BTIBD system in this configuration, it is hard to prepare uniform nanocomposite VO$_x$ films with resistivity in 0.01-10 $\Omega\cdot$cm across a 4” wafer. By using beam blocker may be able to prevent the high energy Ar+ bombard to the substrate and improve film uniformity. However, it might also prevent FCC nanocrystalline domains formation in the deposited films. Further experiments would have to be made at different bias voltages, ppO$_2$ and pulse widths to better determine whether this method is capable of making films in the low resistivity range currently used in microbolometers.

4.6 (Mo/V)O$_x$ thin films properties and thermal stability

It has been shown in previous work using magnetron sputtering that adding molybdenum in the 0.01-1 $\Omega\cdot$cm VO$_x$ thin films prepared by magnetron pulsed-dc sputtering improves the films electrical properties and thermal stability [37]. In order to study the properties of (Mo/V)O$_x$ alloy films prepared by BTIBD system, one Mo target and two vanadium targets were co-sputtered to get alloyed films.

In the experiment, all three targets were powered with -800 V and the pulse frequency was 10 kHz. The two V targets had a pulse width fixed at 1 $\mu$s and the pulse width of the Mo was varied from 30 $\mu$s to 95 $\mu$s in order to control the Mo composition in alloy films. One pure VO$_x$ control film was deposited at the same processing parameters but without Mo target turned on. Figure 4-7 shows the (Mo/O)O$_x$ alloy film deposition rate and electrical properties as a function of Mo pulse width. The Mo to V ratio was measured by EDS with error of ±5%.

When Mo target was turned off, the pure VO$_x$ thin films were deposited. Table 4.1 shows that the deposition rate of alloy films and the Mo content increases when the pulse width of the Mo target decreases (or the sputtering portion of the full duty cycle increases). When the ppO$_2$ is controlled at 1E-6 Torr by the residual gas analyzer feedback controller, the oxygen flow rate
increases with decreasing the pulse width of the Mo target. This indicates that the sputtered Mo species are actively reacting with O\textsubscript{2} in the plasma during deposition. The alloy films resistivity increases when Mo to V ratio increases, and surprisingly when the Mo/V ratio is about 2, the film resistivity is as high as 2E-5 Ω\textperiodcentered cm. However, when the Mo content in the alloy films further increases, it is expected that the films resistivity will eventually drop to a low resistivity corresponding to MoO\textsubscript{x} thin films.

Table 4-1. Mo to V atomic ratio changes as a function of Mo target pulse width. Mo to V atomic ratio was measured by EDS spectrum elemental analysis with ±5\% error.

<table>
<thead>
<tr>
<th>Mo target pulse width (μsec)</th>
<th>Mo/V atomic ratio</th>
<th>O\textsubscript{2} flow rate during deposition (SCCM)</th>
<th>Film deposition rate (Å/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Off</td>
<td>0</td>
<td>3.3</td>
<td>0.50</td>
</tr>
<tr>
<td>95</td>
<td>0.04</td>
<td>3.3</td>
<td>0.51</td>
</tr>
<tr>
<td>90</td>
<td>0.08</td>
<td>3.4</td>
<td>0.57</td>
</tr>
<tr>
<td>70</td>
<td>0.38</td>
<td>3.5</td>
<td>0.65</td>
</tr>
<tr>
<td>30</td>
<td>1.90</td>
<td>3.8</td>
<td>1.59</td>
</tr>
</tbody>
</table>

The alloy films as well as the pure VO\textsubscript{x} control film were annealed in Ar atmosphere for 10 min at 350°C in order to evaluate their thermal stability at temperatures that they might experience during device processing. Figure 4-8 shows that after annealing, both the VO\textsubscript{x} film and the alloy films resistivity and TCR values do not change dramatically. BTIBD prepared high resistivity VO\textsubscript{x} thin films are amorphous from GIXRD pattern with x value in the range of 2.2-2.4, measured by Rutherford back scattering [72]. Compared to the high resistivity (>1000 Ω\textperiodcentered cm) amorphous VO\textsubscript{x} prepared by magnetron pulsed-dc sputtering without substrate bias, the BTIBD prepared VO\textsubscript{x} shows better thermal stability [41]. This is probably because the BTIBD prepared VO\textsubscript{x} thin films show a relatively high density (3.93g/cm\textsuperscript{3}). The increased density of BTIBD
prepared VO$_x$ thin films may be caused by two reasons: low processing pressure (according to Thornton's structure zone model), and secondary conditioning by Ar$^+$ ions directly bombard to the film during deposition.

By adding Mo in the high resistivity VO$_x$ thin films, the film deposition rate increases dramatically, without significantly changing the films electrical properties and thermal stability. This suggests that the high throughput, high resistivity and high TCR (Mo/V)O$_x$ alloy films could be an alternative sensing material in vertically integrated pixel microbolometers. However, the electrical noise of these alloy films needs to be further investigated.

![Graph](image)

Figure 4-7. (Mo/V)O$_x$ alloy films deposition rate and resistivity change as a function of Mo content. The red numbers are the TCR values. The ppO$_2$ is fixed at 1E-6 Torr.
Figure 4-8. Resistivity and TCR values comparison before anneal and after 10 minutes anneal in Ar atmosphere for 350°C.

Figure 4-9 plots TCR versus resistivity for VOₓ films prepared by different techniques. The VOₓ and (Mo/V)Oₓ films with resistivity higher than 1E3 Ω•cm and TCR higher than -4 %/K can be reproducibly fabricated using BTIBD. High resistivity VOₓ thin films prepared by BTIBD show higher TCR and better thermal stability than VOₓ and a-Si:H films [43] prepared by other techniques.
Figure 4-9. TCR versus resistivity of VO$_{\text{x}}$ prepared by different methods as well as a-Si:H prepared by PECVD [3],[42].

4.7 1/f noise of high TCR VO$_{\text{x}}$ films and through-film resistor structure for uncooled microbolometers

As mentioned Chapter 1, the conventional uncooled microbolometer pixel structure uses a lateral resistor configuration. Higher resolution requires smaller pixels (state-of-art pixel size is 17 μm×17 μm). However, smaller pixels result less responsivity due to smaller area for absorbing photons. In order to increase the active layer responsivity, higher TCR is desired. Unfortunately,
higher TCR materials inevitably have higher resistivity and 1/f noise. For a lateral resistance structure, the higher resistance of the sensing materials leads to higher Johnson noise, which may limit the microbolometers performance. Hence, a vertical resistor structure has been proposed which is capable of using high resistivity, high TCR sensing materials without introducing high electrical noise associated with high resistance [72]. Figure 4-10 shows the cross-section schematics of conventional lateral structure and vertical structure [72].

![Diagram](image)

Figure 4-10. The left is the conventional lateral resistance pixel design and the right is the new vertical resistance pixel design [72].

The through-film devices made with BTIBD prepared VO\textsubscript{x} have been reported by Basantani et al. in 2013. To measure the through-film resistivity, TCR, and also electrical noise of the BTIBD prepared VO\textsubscript{x} films, the films were patterned by photolithography. The VO\textsubscript{x} resistivity was extracted from the resistance measurement of different contact areas between top and bottom metal contacts. As shown in Figure 4-11, the deposited VO\textsubscript{x} film resistance increases linearly with "1/contact area", and the through-film resistivity is equal to the slope of the line divided by film thickness. For the same VO\textsubscript{x} material, the measured through-film resistivity is 30% higher than the lateral-film resistivity. One reason for this might be that there is a high resistivity intermixed layer of TiO\textsubscript{2} between bottom Ti metal and deposited VO\textsubscript{x}. However, the measured TCR and normalized Hooge's parameter $\alpha H/n$ are the same for both the lateral and through-film configuration. Figure 4-12 shows the normalized Hooge's parameter versus TCR values of VO\textsubscript{x} prepared by different methods, as well as other sensing materials for bolometers developed by our group. It again shows the general trend that higher TCR VO\textsubscript{x} films have higher
1/f noise in addition to higher resistivity as mentioned previously. Compare to PECVD prepared a-Ge and a-Si, at the same TCR range, BTIBD prepared VO$_x$ show lower 1/f noise, suggesting possible higher NETD and better performance.

Figure 4-11. BTIBD prepared VO$_x$ through-film resistance change as a function of 1/contact area [72].
Figure 4-12. Normalized Hooge's parameters versus TCR of VO$_x$ prepared by different methods, replotted from Ref [72].

4.8 Conclusion

In this Chapter, VO$_x$ thin films with TCR $<$-4.5%/K in the resistivity range of 1E3 to 1E5 $\Omega \cdot$cm have been reproducibly deposited by using the BTIBD system. Different processing parameters such as oxygen partial pressure, oxygen inlet position, processing pressure, target bias voltage, and pulse width and their effect on the electrical properties of VO$_x$ thin films has been investigated. Mo doped VO$_x$ thin films show much higher deposition rates and good thermal stability when compared with similar resistivity undoped VO$_x$ thin films. BTIBD prepare VO$_x$ films show higher TCR and lower 1/f noise compared to other high TCR materials. The results
suggest that BTIBD prepared VO$_x$ are possible better candidates to next generation of uncooled focal plane arrays that would incorporate through-film resistive bolometer structures.

Though high TCR (<4.5 %/K) VO$_x$ can be easily made in this BTIBD system, it is hard to prepare uniform nanocomposite VO$_x$ films with resistivity in 0.01-10 Ω•cm. The previous study [37] and the result in this Chapter show that adding Ni and Mo in VO$_x$ thin films did not significantly affect the electrical properties of the deposited VO$_x$ thin films. This led to further investigation into the bolometric properties of NiO$_x$ and MoO$_x$, which would be further detailed in Chapter 5.
Chapter 5

Nickel Oxide and Molybdenum Oxide Thin Films Prepared by Biased Target Ion Beam Deposition

As discussed in Chapter 4, using BTIBD, it is hard to deposit uniform vanadium oxide thin films which have a resistivity in the range of 0.01 to 10 $\Omega \cdot \text{cm}$ typical of what is used currently in IR microbolometer applications. In this chapter, biased target ion beam deposited (BTIBD) nickel oxide (NiO$_x$) and molybdenum oxide (MoO$_x$) thin films have been investigated for microbolometer applications. The NiO$_x$ and MoO$_x$ thin film deposition rate, electrical properties, structural and optical properties, as well as thermal stability will be discussed in this Chapter. NiO$_x$ and MoO$_x$ thin film process control and electrical properties will be compared to the VO$_x$ thin films presently used in industry and those discussed in this thesis.

5.1 NiO$_x$ prepared by BTIBD system

5.1.1 Experiment details

NiO$_x$ thin films have been reported as microbolometer active sensing layers. The methods to fabricate NiO$_x$ thin films for infrared imaging include: reactive magnetron pulsed dc sputtering, reactive rf sputtering and heat treatment of sputtered Ni thin films in oxygen atmosphere [9], [10]. Potential advantages of using NiO$_x$ thin films as infrared imaging sensing materials include: 1) low number of phases (NiO and Ni$_2$O$_3$) compared to VO$_x$ which makes it is easy to reproducibly fabricate; 2) resistivity is easy to engineer by controlling the nickel vacancies and oxygen interstitial; 3) fabrication method is cheap and compatible to the CMOS process; 4) relatively low 1/f noise has been reported for a poly-crystalline structure [9].
In this work, NiO\textsubscript{x} thin films were reactively sputter deposited from a 99.99% metallic Ni target in an O\textsubscript{2}/Ar ambient in the BTIBD system. The source and HC Ar flow rate were 80 SCCM and 10 SCCM respectively. The total processing pressure was about 7E-4 Torr. Ion source discharge current and voltage was 7.5 Amp and 45 V. The Ni target was pulsed dc biased at -800 V with 10 kHz pulse repetition rate and 1μsec pulse width. The deposition rate and electrical properties of NiO\textsubscript{x} thin films were studied with a function of the oxygen partial pressure (ppO\textsubscript{2}) and total processing pressure.

To study the NiO\textsubscript{x} film thermal stability, one set of samples was annealed in air on hot plate at 250°C for 10 minutes. The other set of samples was simply stored in sample boxes in the laboratory for 250 days (8 months) with no effort to control the ambient after which the resistivity and TCR were measured. These 250 day-old samples were annealed at 350°C for 20 minutes in an Ar or O\textsubscript{2} ambient, and resistivity and TCR again measured.

5.1.2 NiO\textsubscript{x} thin film deposition rate and electrical properties

NiO has a rock salt crystal structure and is reported to be a p-type semiconductor [73], [74]. Resistivity of NiO\textsubscript{x} thin films can be controlled by adjusting the Ni to O ratio [75], [76]. In this work, the biased target ion beam deposited NiO\textsubscript{x} thin film properties were engineered by varying the ppO\textsubscript{2} from 2E-7 to 6E-6 Torr. As shown in Figure 5-1, as the oxygen partial pressure increases, the deposited NiO\textsubscript{x} thin film deposition rate increases. For NiO\textsubscript{x} deposition, nickel oxidation can occur at the target, in the plasma-filled chamber ambient, and at the substrate. The increase of deposition rate indicates that at a lower oxygen partial pressure, the Ni target is not significantly oxidized yet, and the reaction mainly happens in the plasma ambient or at the substrate. The large increase of NiO\textsubscript{x} resistivity suggests the film changes from Ni rich to a more oxidized state. However, further increase of ppO\textsubscript{2} leads to a decrease in deposition rate which
may be due to an increase in oxidation of the Ni target surface. Further increase in the oxygen partial pressure results in a continued decrease in the deposition rate, indicating increased oxidation of the Ni target surface. Unlike VO$_x$, further increase of oxygen partial pressure leads to a decrease in the NiO$_x$ thin film resistivity; this has been attributed to an increase in the oxygen interstitial concentration [75] [76]. In this work, the as-deposited NiO$_x$ thin film resistivity ranges from 1 to 300 $\Omega$·cm with TCR from -2.2 to -3.3 %/K as the oxygen partial pressure is varied from $6\times10^{-6}$ to $1\times10^{-5}$ Torr. Notably, the NiO$_x$ thin film resistivity varies slowly and monotonically with the oxygen partial pressure in this range and the film characteristics are easily controlled. Compare to BTIBD prepared VO$_x$ thin films discussed in Chapter 4, BTIBD prepared NiO$_x$ thin films show a much larger process latitude with respect to oxygen partial pressure and a better overall deposition rate than VO$_x$ thin films (at a ppO$_2$=2E-6 Torr, the deposition rate of NiO$_x$ from a Ni target is 10 times of VO$_x$ sputtered from a single V target).

![Figure 5-1](image.png)

Figure 5-1. Biased target ion beam deposition prepared NiO$_x$ thin films deposition rates, resistivity and TCR change as a function of ppO$_2$. 
The deposition rate and electrical properties of as-deposited NiO\textsubscript{x} thin films can also be engineered by total processing pressure. In our BTIBD system, the processing pressure is not actively controlled so the total processing pressure is varied by varying the source Ar flow rates. However, by increasing the source Ar flow rates, the end-Hall discharge voltage decreases, as well as the Ar\textsuperscript{+} ion energy which is approximately 60\% of the discharge voltage. A set of experiments was performed where the oxygen partial pressure was fixed at 6E-6 Torr and the source Ar flow rates was varied from 60 to 100 SCCM yielding a processing pressure from 0.6 to 1.6 mTorr. As shown in Figure 5-2, by increasing of the processing pressure, the film deposition rate and the resistivity decreased. The decrease of deposition rate may due to more collision of sputtered species before deposited on the substrate (shorter mean free paths) or a reduced number of Ar ions available for sputtering because of the higher background pressure. The lowest resistivity of as-deposited NiO\textsubscript{x} thin films is about 0.5 \(\Omega\cdot\text{cm}\) with TCR of -2.0 \%/K.

Figure 5-2. BTIBD prepared NiO\textsubscript{x} thin films deposition rates, resistivity and TCR change as a function of total processing pressure.
5.1.3 Aging effects and thermal stability of NiO$_x$ thin films

Aging effects and thermal stability of NiO$_x$ thin films have also been studied. The resistivity and TCR were measured after the as-deposited films were annealed in air on a hot plate at 250$^\circ$C for 10 minutes. Another set of as-deposited films was simply stored in sample boxes in the laboratory with no effort to control the ambient. The resistivity and TCR of the 250 day-old samples were measured. They were also annealed at 350 $^\circ$C for 20 minutes in an Ar or O$_2$ atmosphere, and resistivity and TCR again measured. As shown in Figure 5-3, the NiO$_x$ resistivity and TCR electrical properties change little after 250 days of storage. After annealing at low temperature (250$^\circ$C) for a short time, the film electrical properties do not change much either. However, the changes after inert gas annealing, in either Ar or O$_2$ at 350$^\circ$C for a longer time are very large, with a factor of $10^2$ to $10^4$ increase in film resistivity and a significant increase (40-50%) in TCR. Interestingly, the changes with annealing are similar for both Ar and O$_2$ ambient. The increase in film resistivity and TCR are somewhat larger for annealing in O$_2$ than for Ar, perhaps indicating more complete oxidation. However, the difference that results from the annealing ambient is small compared to the difference between annealed and as-deposited films. This would suggest that the change in NiO$_x$ properties during annealing is probably due to the evolution of the microstructure rather than a change in composition.
Figure 5-3. NiO$_x$ thin film resistivity and TCR values comparison for films that were as-deposited, after exposed to air for 250 days, and after annealing.

5.1.4 Structure analysis of NiO$_x$ thin films

Figure 5-4 shows GIXRD results for as-deposited NiO$_x$ thin films. All the films deposited in the oxygen partial pressure range studied are polycrystalline. As the oxygen partial pressure increases, the GIXRD data suggests that the film texturing and stress change. For oxygen partial pressure from 2E-7 to 5E-7 Torr, the NiO (111) peak increases and is larger than the (200) peak. For larger oxygen partial pressure the (111) peak decreases and the (200) peak dominates. The (200) peak position also moves to smaller angle, which may be due to increasing
stress. To measure the stress in the NiO\textsubscript{x} thin films, film surface curvature was measured by profilometry before and after NiO\textsubscript{x} deposition. The measured average compressive stress of a 56 nm thick NiO\textsubscript{x} prepared at ppO\textsubscript{2}=4E-6 Torr is approximately 800 MPa. The same sample was used to calculate the average grain size. The average grain size was calculated using the Scherrer formula:

\[ L = \frac{K\lambda}{\beta \cos \theta} \quad \text{Eq. 5.1} \]

where \( L \) is average crystallite size, \( \beta \) is the peak width of the diffraction peak profile at half maximum height in \( 2\theta \) axis (in radians), \( \lambda \) is the X-ray wavelength in nanometer, and \( K \) is a constant related to crystallite shape. In this work, \( K \) is taken as 0.9, and \( \lambda \) is 0.15 nm (Cu K\textsubscript{alpha}). Table 5-1 shows the parameters measured by software and the calculated crystallite sizes from three peaks (As shown in Figure 5-5). The average grain size is about 5.7 nm in this film. Similarly, the grain size of this sample after annealing in Ar at 350 °C was also calculated and found to be about 7 nm (Table 5-2). The NiO\textsubscript{x} thin film GIXRD peak intensity and calculated grain size before and after annealing show no significant difference. However, the GIXRD peak position shifts to higher angle, which may due to the stress change in thin film. This stress may be partly responsible for the large increase of resistivity after annealing.
Figure 5-4. GIXRD pattern of as-deposited NiO\textsubscript{x} thin films prepared at different ppO\textsubscript{2}. 
Figure 5-5. GIXRD comparison of a 56-nm-thick NiO$_x$ thin film before and after annealing. This sample was used to calculate the average grain size and average stress. This film was prepared with 60 SCCM source Ar, 4E-6 Torr oxygen partial pressure, and -800 pulsed dc target bias with 100 μsec pulse period and 1 μsec pulse width. Oxygen inlet position was near Ni.

Table 5-1. Parameters from GIXRD measurement and calculated crystallite size of as-deposited NiO$_x$ thin film:

<table>
<thead>
<tr>
<th>Ref Angle (2θ)</th>
<th>Ref (h k l)</th>
<th>Ref d(Å)</th>
<th>Angle (20)</th>
<th>FWHM</th>
<th>Ln(1/cos θ)</th>
<th>Ln(FWHM)</th>
<th>$L_1$(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37.20</td>
<td>(111)</td>
<td>2.4</td>
<td>35.87</td>
<td>1.31°</td>
<td>0.049</td>
<td>-3.779</td>
<td>6.382</td>
</tr>
<tr>
<td>43.23</td>
<td>(200)</td>
<td>2.1</td>
<td>42.03</td>
<td>1.20°</td>
<td>0.068</td>
<td>-3.869</td>
<td>7.118</td>
</tr>
<tr>
<td>62.79</td>
<td>(220)</td>
<td>1.5</td>
<td>60.97</td>
<td>1.37°</td>
<td>0.149</td>
<td>-3.729</td>
<td>6.702</td>
</tr>
</tbody>
</table>

Table 5-2. Parameters from GIXRD measurement and calculated crystallite size of NiO$_x$ thin film annealed in Ar at 350°C for 20 min:

<table>
<thead>
<tr>
<th>Ref Angle (2θ)</th>
<th>Ref (h k l)</th>
<th>Ref d(Å)</th>
<th>Angle (20)</th>
<th>FWHM</th>
<th>Ln(1/cos θ)</th>
<th>Ln(FWHM)</th>
<th>$L_1$(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37.20</td>
<td>(111)</td>
<td>2.4</td>
<td>36.79</td>
<td>1.25°</td>
<td>0.052</td>
<td>-3.822</td>
<td>6.68</td>
</tr>
<tr>
<td>43.23</td>
<td>(200)</td>
<td>2.1</td>
<td>42.89</td>
<td>1.15°</td>
<td>0.071</td>
<td>-3.906</td>
<td>7.41</td>
</tr>
<tr>
<td>62.79</td>
<td>(220)</td>
<td>1.5</td>
<td>62.47</td>
<td>1.30°</td>
<td>0.156</td>
<td>-3.786</td>
<td>7.15</td>
</tr>
</tbody>
</table>

5.1.5 Optical properties of NiO$_x$ thin films

The optical properties of as-deposited NiO$_x$ were extracted from ex-situ ellipsometry measurement. Ellipsometric spectra were collected at room temperature at an angle of incidence of 70° using a dual rotating compensator multichannel instrument. Least squares regression analysis with an unweighted error function were combined to fit experimental ellipsometric spectra to a structural model consisting of a semi-infinite crystal silicon (c-Si) wafer substrate, ~100 nm of thermally grown silicon dioxide (SiO$_2$), NiO$_x$ bulk thin film, and surface roughness. The optical response of the surface roughness layer is represented using a Bruggeman effective
medium approximation consisting of fixed 0.5 NiO₅ bulk film and 0.5 void volume fractions. The surface roughness for all these NiO₅ samples are less than 2 nm. As shown in Figure 5-6(a), the ex-situ refractive index n and extinction coefficient k of as-deposited NiO₅ prepared at different ppO₂ were compared. At 633nm, the refractive index of as-deposited NiO₅ ranges from 2.43 to 2.35 with ppO₂ from 1E-6 to 6E-6 Torr. Absorption coefficient (Figure 5-6 (b)) was calculated by equation \( \alpha = 4\pi k / \lambda \) where \( k \) is the extinction coefficient and \( \lambda \) is the wavelength of incident light.

At low energy (<3 eV), the observed \( \alpha \) for NiO₅ increases in amplitude with increasing oxygen partial. Similar to semiconducting VOₓ [77], the amplitude of the absorption coefficient for NiO₅ decreases with increasing resistivity. The optical properties for NiO₅ films prepared here fall within the range reported in literature [78], [79]. Significant absorption below the reported NiO band gap near 3.0-4.0 eV is observed and indicates that non-stoichiometry may give rise to multiple Ni valence states in the film [78], [80]–[82].

The optical properties of NiO₅ before and after annealing have been also investigated. The same sample (NiO₅ 56 nm thick) which was described in last section was analyzed by ex-situ SE before and after annealing in Ar or O₂ at 350 °C for 20 min, respectively. Figure 5-7 shows that after annealing, the absorption coefficient at lower energy levels decreases, corresponding to the previous observation: \( \alpha \) decreases with increasing film resistivity. However, there is no difference between \( \alpha \) of NiO₅ annealed in Ar and O₂, which agrees the previously mentioned observation for annealing that the film resistivity has little difference after annealing in Ar or O₂.
Figure 5-6. Plot of (a) $n$ and $k$ versus $hv$ and, (b) absorption coefficient $\alpha$ versus $hv$ for as-deposited NiO$_x$ thin films prepared at different ppO$_2$, compared to atomic layer deposited (ALD) NiO [78].
Figure 5-7. Plot of $\alpha$ versus $h\nu$ for as-deposited NiO$_x$ thin films, after annealed in Ar, and annealed in O$_2$ at 350°C for 20 min. Reference from [78]

5.2 MoO$_x$ thin films prepared by BTIBD system

In chapter 4, it was shown that for high resistivity and high TCR VO$_x$ films, the addition of large amount of Mo in the VO$_x$ thin films did not significantly change the electrical properties of the films. This section describes experiments designed to determine whether pure MoO$_x$ thin films can be used as a potential microbolometer sensing material.
5.2.1 Experimental details

MoO\textsubscript{x} thin films were deposited on thermally oxidized silicon substrates by the BTIBD system using a mixture of Ar and O\textsubscript{2}. Molybdenum (Mo) target with 99.99\% purity were pulsed dc biased at -800 V with 10 kHz pulse repetition rate and 1\(\mu\)sec pulse width. The ion source discharge current was held at 7.5 Amp and the ion beam current was about 1.5 Amp, and the ion source discharge voltage was kept below 45 V. The ion source Ar flow rate is 80 SCCM and HC flow rate is 10 SCCM, whereas the processing pressure was about 0.7 mTorr.

As with the nickel oxide films described in the previous section, to investigate the deposited films thermal stability, the resistivity and TCR values were measured again after MoO\textsubscript{x} films were exposed to natural atmosphere for 250 days. In addition, these 250-day-old samples were measured again after being annealed in the RTA system at 350 °C in Ar atmosphere for 20 minutes.

5.2.2 MoO\textsubscript{x} thin films electrical properties

MoO\textsubscript{x} thin films were reactively sputter deposited from a 99.99\% metallic Mo target in an O\textsubscript{2}/Ar ambient in the biased target ion beam deposition system. The oxygen partial pressure was varied from 1E-6 to 2E-6 Torr. As shown in Figure 5-8, as the oxygen partial pressure increases, the deposited MoO\textsubscript{x} thin film resistivity increases from 3E-4 to 2000 Ω·cm. For MoO\textsubscript{x} deposition, molybdenum oxidation can occur at the target, in the plasma-filled chamber ambient, and at the substrate [60]. When the oxygen partial pressure is low (1E-6 Torr), the deposited films are metallic (3E-4 Ω·cm resistivity and small, positive TCR). When the oxygen partial pressure increases to 1.3E-6 Torr, the MoO\textsubscript{x} resistivity increases to 3 Ω·cm with a negative TCR of -2.2%/K. Figure 5-8 shows that the film deposition rate approximately doubles as the oxygen
partial pressure increases from 1E-6 Torr to 1.3E-6 Torr. The increase in deposition rate suggests that the Mo target surface is not significantly oxidized and most of the oxidation takes place either in the chamber ambient or at the substrate. Further increase of oxygen partial pressure leads to increasing film resistivity and TCR, and decreasing deposition rate. The deposited film resistivity increases slowly with increasing oxygen partial pressure and thus allows easier control of film resistivity in the region of interest. This is in contrast to VOₓ films deposited in our biased target ion beam deposition system, where the deposited film resistivity changes from metallic (3E-4 Ω•cm) to high resistivity (>1000 Ω•cm) for an oxygen partial pressure change of <1E-7 Torr. The decrease in deposition rate for oxygen partial pressure >1.3E-6 Torr is likely due to the reduced sputter yield as the molybdenum target surface becomes increasingly oxidized.

Figure 5-9 shows that similar to the VOₓ and NiOₓ thin films, the MoOₓ thin films show a linear decrease of log (Resistance) with increasing of temperature from 290 K to 350 K, suggesting MoOₓ thin films are also potential candidates for bolometer applications. They have the addition advantages of having a much higher deposition rate than that of VOₓ.

Figure 5-8. Deposition rate and electrical properties of MoOₓ with different ppO₂
Figure 5-9. Plot of Log(R) vs. Temperature, MoO$_x$ prepared with different ppO$_2$.

5.2.3 Aging effects and thermal stability of MoO$_x$ thin films

The resistivity and TCR of the MoO$_x$ thin films was measured after deposition and again after 250 days. Similar to the NiO$_x$ samples, during this time the samples were simply stored in sample boxes in the laboratory with no effort to control the ambient. The 250 day-old samples were also annealed at 350°C for 20 minutes in an Ar ambient, and resistivity and TCR again measured. As shown in Figure 5-10, similar to NiO$_x$ thin films, the MoO$_x$ resistivity and TCR electrical properties change little after 250 days of storage. However, the changes after inert gas annealing are very large, with a factor of $10^3$ to $10^4$ increase in film resistivity. Films with the highest resistivity had non-linear contacts and it was therefore hard to measure TCR; for films
with lower resistivity, TCR increases by about 25 % after the inert gas anneal, which is not as much as seen for NiO$_x$ films. Annealing in oxygen ambient may lead to more complete oxidation and higher film resistivity of MoO$_x$ films, which is not desirable for microbolometer applications.

5.2.4 Structure analysis of MoO$_x$ thin films

Figure 5-11 shows the GIXRD pattern of as-deposited MoO$_x$ thin films prepared at different oxygen partial pressures. As shown in Figure 5-11, for an oxygen partial pressure of 1E-
6 Torr, the metallic sample has peaks corresponding to MoO$_2$, but shifted from the expected position. The shift of the peaks suggests significant stress developed in the deposited thin film. MoO$_2$ is metallic with a low resistivity about 1E-4 Ω•cm [83], [84] so the combination of film resistivity and x-ray characterization indicate that this film is either MoO$_2$ or a mixture of MoO$_2$ and Mo. As the oxygen partial pressure is increased, the MoO$_2$ peaks decrease and peaks corresponding to MoO$_3$ appear. The MoO$_3$ peaks are broad, indicating small grain size, possibly in an amorphous matrix. The GIXRD characteristics change little with further increase in oxygen partial pressure, consistent with previous reports that showed little change in thin film x-ray characteristics for sputtering over a range of large oxygen partial pressure [83], [85], [86]. Although the x-ray characteristics change little, the film resistivity increases from 0.9 to 2000 Ω•cm as the oxygen partial pressure increases from to 1.3E-6 to 2E-6 Torr.

![GIXRD pattern of as-deposited MoOx thin films prepared at different oxygen partial pressures. The reference peaks in this picture are corresponding to MoO$_2$ (Tetragonal) and MoO$_3$ (Monoclinic). The peak at 54° with the oxygen partial pressure of 1E-6 and 1.7E-6 Torr is believed due to Si substrate.](image_url)
5.2.5 Optical properties of MoO$_x$ thin films

The as-deposited MoO$_x$ thin films optical properties were deduced by the ex-situ SE measurement. As shown in Figure 5-12, MoO$_x$ film prepared at oxygen partial pressure at 1E-6 Torr exhibits a Drude feature, indicating the metallic behavior. This observation agrees the film low resistivity (3E-4 Ω•cm).

All MoO$_x$ films prepared at oxygen partial pressure >1.0E-6 Torr in this work do not exhibit a Drude feature, indicating semiconductor like behavior. Negative values of TCR for these films are consistent with this observation. These MoO$_x$ film refractive index at 633 nm varies from 1.7 to 2.3 as the oxygen partial pressure increases from 1.3E-6 to 2.0E-6 Torr, which is similar to a previous report [87]. As shown in Figure 5-12(b), there is significant absorption at photon energy from 3.5 to 4.2 eV, which is similar to the reference. There is also absorption at photon energy <3.0 eV, and the absorption coefficient $\alpha$ decreases in amplitude with increasing oxygen partial pressure. Film resistivity also increases with oxygen partial pressure for MoO$_x$ in this range. A similar feature has been observed in disordered mixed valence VO$_x$ thin films, which also decreases in amplitude with increasing film resistivity [77], [88]. Although different trends are observed between oxygen partial pressure and film resistivity for these MoO$_x$ and NiO$_x$ films, the behavior of the low energy feature in the optical properties correlates with film resistivity for both cases. The low energy absorption of non-stoichiometric MoO$_x$ may indicate that the feature originates from a distribution in the valence states of Mo. These low energy absorption features support the idea that mixed-valence states are present, considering that the band gap of MoO$_3$ has been reported near 2.9-3.4 eV [87][89], and MoO$_2$ is metallic [90].
Figure 5-12. Plot of (a) $n$ and $k$ versus $h\nu$ and, (b) absorption coefficient $\alpha$ versus $h\nu$ for as-deposited MoO$_x$ thin films prepared at different ppO$_2$ [87].
5.3 1/f noise measurement

To evaluate the 1/f noise of BTIBD prepared NiO$_x$ thin films, one NiO$_x$ sample with resistivity was prepared at an oxygen partial pressure of 4E-6 Torr. The measured film resistivity is 29.7 $\Omega \cdot$cm with a TCR of -2.5%/K. The calculated normalized Hooge’s parameter of this sample is 6.58E-19 cm$^3$.

Figure 5-13 shows the normalized Hooge’s parameter comparison of various sensing materials investigated by our group. The 1/f noise of BTIBD prepared NiO$_x$ is larger than that of VO$_x$, and is similar to PECVD a-Si. Other group reported the k value of 1/f noise of reactive sputtered NiO$_x$ thin film was 9.7E-12 with a resistivity of 33.6 $\Omega \cdot$cm and TCR of -3.33%/K [91]. However, the volume information of this sample was not included in the report. Thus, no direct comparison to the BTIBD prepared NiO$_x$ film can be made.

Figure 5-13. TCR versus normalized Hooge’s parameter comparison among: VO$_x$ prepared by ion beam deposition, pulsed dc magnetron sputtering, biased target ion beam deposition, PECVD a-Si, PECVD a-Ge, and BTIBD NiO$_x$. 
5.4 Conclusion

In this Chapter, high TCR NiO$_x$ and MoO$_x$ thin films were prepared by our biased target ion beam deposition system. The deposition rate and electrical properties of as-deposited NiO$_x$ and MoO$_x$ thin films are dependent on processing parameters such as the oxygen partial pressure and processing pressure. The resistivity of as-deposited NiO$_x$ thin films is 1 to 300 $\Omega \cdot \text{cm}$ with a temperature coefficient of resistance (TCR) from -2.2 %/K to -3.3 %/K; the resistivity of as-deposited MoO$_x$ thin films is 3 to 2000 $\Omega \cdot \text{cm}$ with TCR from -1.7 %/K to -3.2 %/K. Figure 5-13 shows TCR versus resistivity for a variety of thin films. NiO$_x$ and MoO$_x$ show comparable bolometric properties to device-grade VO$_x$ in the resistivity range of 0.1 to 100 $\Omega \cdot \text{cm}$. Compared to BTIBD prepared VO$_x$, the resistivity for both NiO$_x$ and MoO$_x$ varies slowly over a relatively large range of oxygen partial pressure, permitting easier control of film characteristics than for VO$_x$ thin films. XRD characteristics and optical absorption analysis suggests that both the NiO$_x$ and MoO$_x$ thin films show short range order and are semiconductor. The thermal stability of NiO$_x$ and MoO$_x$ thin films was also studied. The result shows that both NiO$_x$ and MoO$_x$ thin films show good long term stability in natural atmosphere. After rapid thermal annealing, both NiO$_x$ and MoO$_x$ electrical properties change significantly. The NiO$_x$ properties after annealing in Ar as compared to O$_2$ do not show dramatic difference, indicating that the change in properties during annealing is probably due to the evolution of the microstructure rather than a change in composition. In order to use NiO$_x$ and MoO$_x$ thin films as microbolometer sensing materials, the annealing effects on the film properties should be further investigated.
Figure 5-14. Resistivity versus TCR comparison among: VO_x prepared by ion beam deposition, pulsed dc magnetron sputtering, biased target ion beam deposition, and biased target ion beam deposited NiO_x and MoO_x.
Chapter 6

Conclusion

6.1 Conclusion

Nanocomposite vanadium oxide thin films with properties suitable for microbolometer devices have been prepared by reactive magnetron pulsed-dc sputtering with substrate bias. Reactive magnetron sputtering from a metallic V target is an inherently non-uniform process due to target hysteretic characteristics and the non-uniform oxidization across target surface. The hysteretic oxidation of the V target surface was assessed by measuring the average cathode current under different total \( \text{O}_2/\text{Ar} \) flow rates, processing pressure, and target-to-substrate distance. Non-uniform oxidation of the V target surface was analyzed by Raman spectroscopy. The \( \text{VO}_x \) thin film deposition rate, resistivity, and TCR values were greatly affected by the oxygen to Ar inlet ratio, processing pressure, throw distance, and the geometry of the delivery of reactive gas. The target hysteresis curve suggests that lower processing pressure leads to a more gradual transition of the V target surface oxidation which translates into better control of deposited film properties in the transition region of the hysteresis loop. It was found that a larger throw distance and an oxygen inlet near the substrate improve the as-deposited \( \text{VO}_x \) uniformity and process control. However, lower processing pressure and longer throw distance result in lower deposition rate. The overall conclusion for magnetron sputtered films is that once processing conditions are well understood and characterized, the deposited nanocomposite \( \text{VO}_x \) thin films show comparable bolometric properties to commercial ion beam deposited \( \text{VO}_x \). These results suggest that reactive pulsed-dc magnetron sputtering can be an industrial alternative for depositing \( \text{VO}_x \) films for microbolometers and potentially offer advantages in terms of deposition rate and machine costs of a magnetron sputter system over one using an ion beam.
In Chapter 3, co-sputtering from a pure V target and a V$_2$O$_5$ target in the magnetron sputtering system was also investigated. Similar to reactive sputtering from a metallic V target, VO$_x$ thin film TCR/resistivity was improved by applying 25 W substrate bias during the co-sputtering process. By varying the oxygen to Ar ratio, the film deposition rate was 35% higher than the one sputtered from a single V target, and the film uniformity was also improved. VO$_x$ thin films prepared by co-sputtering from a V and V$_2$O$_5$ target showed comparable bolometric properties to VO$_x$ prepared by IBD.

Other variations of magnetron reactive sputtering to deposit VO$_x$ films were also explored for example, sputtering from a VC target, sputtering of a V$_2$O$_5$ or a V$_2$O$_x$ target with various substrate biases, and reactive sputtering from a V target with H$_2$, O$_2$, and Ar mixtures. However, the results for the limited experiments performed did not indicate that these offered any advantages for fabricating VO$_x$ thin films for microbolometer applications, due to either low deposition rate or limited TCR/resistivity combination.

In Chapter 4, a new method for making VO$_x$ films was introduced BTIBD. High TCR (<-4.5%/K) high resistivity (1E3 to 1E5 Ω•cm) VO$_x$ thin films were produced by the biased target ion beam deposition system. Compare to the high TCR (<-4%/K) VO$_x$ films prepared by magnetron sputtering, the BTIBD prepared VO$_x$ films had lower room temperature resistivity. Due to the low processing pressure (<1 mTorr) and the secondary condition of Ar+ ions to the substrate, these BTIBD prepared high TCR VO$_x$ films were denser than their counterparts prepared by magnetron sputtering, and hence had better thermal stability. The addition of Mo in VO$_x$ thin films significantly increased film deposition rate, which is desirable for commercial preparation of microbolometer sensing films. After annealing, the high TCR (Mo/V)O$_x$ thin film electrical properties changed little, suggesting good thermal stability. GIXRD results indicated that high TCR VO$_x$ and (Mo/V)O$_x$ thin films were x-ray amorphous. These high TCR high resistivity VO$_x$ and (Mo/V)O$_x$ thin films have the potential to be used as the sensing materials for
a through-film microbolometer pixel design. By using the through-film pixel design, high TCR 
VO_x can be utilized without introducing high Johnson noise, which is usually correlated to film 
resistance.

Although in the BTIBD system many processing parameters can be varied to engineer the 
deposited film properties, unfortunately, making films in the 0.1-10 Ω•cm range proved to be 
difficult. By increasing the oxygen partial pressure less than 1E-7 Torr, the VO_x film resistivity 
increased abruptly from 1E-4 Ω•cm to over 1000 Ω•cm. Other processing parameters such as the 
vanadium target bias voltage, pulse width, total processing pressure have been varied, however, it 
was still difficult to produce uniform VO_x thin films in the range of 0.01 to 10 Ω•cm.

Due to the difficult process control encountered for magnetron sputtering and BTIBD of 
VO_x thin films, other metal oxide thin films such as NiO_x and MoO_x thin films were investigated 
as potential microbolometer imaging layer materials as detailed in Chapter 5. BTIBD prepared as-
deposited NiO_x thin film resistivity varied from 1 to 300 Ω•cm with TCR from -2.2 to -3.3 %/K, 
and as-deposited MoO_x thin film resistivity was found to vary from 3 to 2000 Ω•cm with TCR 
from -1.7 to -3.2 %/K. Similar to VO_x thin films, higher room temperature resistivity MoO_x and 
NiO_x films showed higher TCR values. BTIBD prepared NiO_x and MoO_x have TCR comparable 
to VO_x in the resistivity range of 0.1 to 100 Ω•cm.

GIXRD and spectroscopic ellipsometry were used to study the structure and optical 
properties of BTIBD prepared MoO_x and NiO_x thin films with different oxygen partial pressure. 
GIXRD results indicated that the room temperature resistivity of as-deposited MoO_x were 
amorphous. By increasing the oxygen partial pressure, the as-deposited MoO_x thin film structure 
appeared to change from MoO_2 to MoO_3, and the MoO_3 peaks were broad. Though GIXRD 
characteristics changed little with further increasing of oxygen partial pressure, the room 
temperature resistivity of the as-deposited film increased over 2000 times. GIXRD results 
indicated that the as-deposited NiO_x films were polycrystalline. The film texture changed and the
compressive stress increased with an increase oxygen partial pressure, all other parameters remaining the same.

The optical properties extracted from the ellipsometry measurement suggested that the MoO\textsubscript{x} prepared at low oxygen partial pressure (1E-6 Torr) had metallic like feature, and MoO\textsubscript{x} prepared at higher oxygen partial pressure showed semiconductor like behavior. The absorption coefficient \( \alpha \) at low energy (< 3eV) decreased with increasing of resistivity and oxygen partial pressure. Similar to semiconducting MoO\textsubscript{x} and VO\textsubscript{x}, the amplitude of the low energy feature for NiO\textsubscript{x} decreases with increasing resistivity. Both of the BTIBD prepared semiconducting MoO\textsubscript{x} and NiO\textsubscript{x} optical index fell within the range reported in literatures. However, significant absorption below the reported band gap for both MoO\textsubscript{x} and NiO\textsubscript{x} indicated the existence of multiple valence states of Mo and Ni in the films.

Notably, by using the reactive BTIBD method, NiO\textsubscript{x} and MoO\textsubscript{x} thin film deposition had a much larger process window than VO\textsubscript{x} in the regions with properties of interest for microbolometers. As mentioned earlier, process control was very difficult for low resistivity VO\textsubscript{x} thin films deposited by reactive biased target ion beam deposition; films transitioned from metallic to high resistivity with a very small change in oxygen partial pressure. By contrast, MoO\textsubscript{x} and NiO\textsubscript{x} film properties were easily varied by controlling the oxygen partial pressure, and it was expected that process control for other deposition techniques such as diode or magnetron sputtering to be simpler for MoO\textsubscript{x} and NiO\textsubscript{x} than for VO\textsubscript{x}. Measurement of aging effects suggested both MoO\textsubscript{x} and NiO\textsubscript{x} electrical properties have good long term stability. After annealing, MoO\textsubscript{x} film resistivity increased significantly with TCR increasing only 25%. Similar to MoO\textsubscript{x}, NiO\textsubscript{x} film resistivity increased \(~1000\) times after annealing, but the TCR values also doubled. GIXRD showed that the annealing had little change in NiO\textsubscript{x} film microstructure, but significant change in film stress. In the same TCR range, he measured 1/f noise of one NiO\textsubscript{x}
sample was similar to that of PECVD a-Si, and higher than that of VO\textsubscript{x}. The simple process control and the high TCR make MoO\textsubscript{x} and NiO\textsubscript{x} films of interest for microbolometer applications.

### 6.2 Future work

In this thesis it has been shown that reactive pulsed-dc magnetron sputtering can be an industrial alternative for depositing VO\textsubscript{x} films for microbolometers provided the system is well understood and the processing parameters carefully monitored. The study of throw distance effects on deposited films properties was at fixed pressure (5 mTorr). It would be interesting to see how the throw distance affects the target hysteresis behavior and the deposited VO\textsubscript{x} films properties at lower processing pressure (1 mTorr). As shown in this work, lower processing pressure leads to more gradual oxidation of the V target, but also results in lower deposition rate. However, the combination of the shorter throw distance and lower processing pressure may provide both good process control and relatively good deposition rate, which will be a useful guide for incorporating a VO\textsubscript{x} deposition process using a magnetron sputtering system in the commercial microbolometer industry.

Vanadium oxide thin films prepared by reactive magnetron co-sputtering from a V and V\textsubscript{2}O\textsubscript{5} targets have shown preliminary interesting results: comparable resistivity/TCR combination to IBD prepared VO\textsubscript{x}, higher deposition rate, and improved film uniformity. In this work, the V target was pulsed-dc biased was fixed at 300 W whereas the V\textsubscript{2}O\textsubscript{5} target was rf-biased at 200 W, and the total processing pressure was at 5 mTorr. The V:O ratio in the plasma and in the film during deposition can be further tailored by varying the power supplied to these two targets, the O\textsubscript{2} to Ar inlet ratio, and the total processing pressure. It may be possible to optimize the processing parameters and reach good process uniformity, high throughput, and good repeatability.
It has been shown that the process control is difficult for preparing VO$_x$ in the range of 0.01-10 Ω•cm by uniform sputtering from V target, either in an RF diode system [92] or a BTIBD system. However, in all these systems, the oxygen supply was controlled either by fixed oxygen gas flow rates or fixed oxygen partial pressure during the deposition. As shown in Figure 6.1, a preliminary study in our group on an RF diode system showed that at a 2.5% oxygen supply content, the oxygen partial pressure increased by approximately 100%. A similar phenomenon has been observed in the BTIBD system: at a fixed oxygen partial pressure, the oxygen flow rate changed during the deposition. This may be the reason that it is hard to repeatedly produce VO$_x$ in the range of 0.01-10 Ω•cm. One way to overcome this problem would be to employ a closed-loop control between the feed in oxygen content and the target cathode current (target surface oxidation) or film deposition rate (deposited film composition). In addition to the oxygen supply, the target power/voltage, and pulse width/frequency could also be used to closed-loop to better control the deposition process.
Figure 6-1. RGA measured oxygen partial pressure changes as a function of oxygen supply content (gas flow rates ratio of O$_2$/(O$_2$+Ar), the Ar flow rate was fixed at 62 SCCM). (Plotted by Haoyu Li, measured in a rf diode system)

The 1/f noise behavior of BTIBD prepared high TCR high resistivity VO$_x$ thin films has been studied and compared to PECVD prepared high TCR a-Ge and a-Si thin films by our group [48]. However, high TCR (Mo/V)O$_x$ thin films through-film resistivity, TCR and 1/f noise have not been investigated yet. Since (Mo/V)O$_x$ thin films have good thermal stability and much higher deposition rate than pure VO$_x$ thin films, it is suggested that future work compare the 1/f noise of (Mo/V)O$_x$ thin films to other high TCR materials as candidates for next generation high sensitivity microbolometer with through-film structure pixels.

BTIBD prepared high TCR MoO$_x$ and NiO$_x$ have shown comparable TCR/resistivity combination to IBD prepared VO$_x$ thin films. However, due to the off-axis geometry in our BTIBD system, the deposition rate is relatively low. Since the process control of NiO$_x$ and MoO$_x$ electrical properties was easy by varying oxygen partial pressure, it would be promising to prepare MoO$_x$ and NiO$_x$ by rf diode or magnetron sputtering, or in a BTIBD system that was optimized for throughput by having the substrate parallel to the target. Even though the GIXRD characteristics showed that no significant change of NiO$_x$ thin film microstructure before and after annealing, cross-section SEM or TEM might be useful to further understand the microstructure evolution by annealing. The measured 1/f noise of a NiO$_x$ was similar to a-Si. However, as one of the important bolometric properties, the 1/f noise of MoO$_x$ and NiO$_x$ thin films should be further extensively studied. The correlation between MoO$_x$/NiO$_x$ film 1/f noise to the material composition, microstructure, and band structure should be investigated. It will be interesting to see how the 1/f noise of MoO$_x$ and NiO$_x$ effects by different processing parameters and post-annealing treatment.

Thin NiO$_x$ and MoO$_x$ films have been reported as useful hole injection layers for organic light-emitting diodes (OLED) [93], [94],[95] and anode buffer layers in organic photovoltaic cells
to improve device efficiency and stability. The BTIBD prepared NiO$_x$ and MoO$_x$ thin films are potentially interesting for this application. They have a large range of electrical properties, ultra-smooth film surface over a broad range of composition (<2 nm), and good long term electrical properties stability. Due to these properties, it would be interesting to investigate the structural and electrical functionality of BTIBD prepared NiO$_x$ and MoO$_x$ in OLED and OPV devices.
Appendix A

Lithography Steps to Pattern NiO$_x$ Thin Films

2. Spin 495 PMMA C4 at 4000 rpm for 30 sec (~1micron).
3. Bake at 160°C for 10 min.
4. Spin 1811 photoresist at 4000 rpm for 40 sec (~1 micron).
5. Soft bake at 90°C for 90 sec.
6. Use bright field active layer isolation mask and exposure for 50 sec.
7. Reverse bake in NH$_3$ at 90°C for 60 min.
8. Put samples under flood exposure for 75 sec.
9. Develop in 5:1 DI water:351 solution for about 40 sec or until appropriately developed, rinse with DI water and blow dry.
10. Remove residual resist at 1811 and PMMA interface by using oxygen RIE for 3 min.
11. Expose the sample under deep UV for 400 sec.
12. Develop in toluene for 1 min and blow dry.
13. Remove residual resist between PMMA and oxide layer below.
15. Lift off in acetone, rinse with IPA and blow dry.
16. Spin LOR 5B at 4000 rpm for 40 sec.
17. Bake at 160°C for 5 min.
18. Spin 1811 photoresist at 4000 rpm for 45 sec.
20. Use top metal liftoff mask align, and expose for 53 sec.
21. Develop in 3.5:1 DI water: 351 solution for 90 sec or until appropriately developed (see double line), rinse with DI water and blow dry.
22. Sputter deposit 100 nm of Ti.

23. Anneal sample at 120°C for 5 min.

Appendix B

Study of BTIBD System Processing Parameters Effects

As mentioned in Chapter 2, in this 4-Wave LANS BTIBD system, the ion source, the biased targets, and reactive gas partial pressure can be independently controlled. In this section, processing parameters of the ion source and the biased targets are investigated. Target bias current is used to evaluate the process stability.

First, the discharge current and the ion source Ar flow rate effects on the ion source discharge bias and target bias current were studied. In this system, the ion source discharge power supply was set at the constant-current mode of operation and the highest discharge voltage could not exceed 100 Volts (the average ion beam energy is lower than 60 eV).

In this set of experiments, the working gas was Ar and three targets (V, Si, and Ti) were biased. The neutralizer (Neut.) keeper current was set to 1.5 Amp and Neut. bias current was 0.5 Amp higher than the ion source discharge current (keep the plasma neutralized). The applied power on all three biased targets was -800 Volts and the pulse width was 1 µsec, whereas the pulse period was 100 µsec (10 kHz pulse frequency).

Figure B-1 shows the discharge voltage and target bias current change as a function of the discharge current.
Figure B-2. HC Ar flow rate is 9 SCCM, source Ar flow rate is 60 SCCM and oxygen flow rate is 0 SCCM. The total pressure is around 0.7 mTorr. The discharge voltage and target bias current change as a function of discharge current.

Figure B-1 shows that with a fixed ion source Ar flow rate (60 SCCM), the discharge voltage increases as the ion source discharge current increases. Increasing the discharge current also leads to an increase in the target bias current. When discharge current varies from 0.5 Amp to 9.5 Amp, the target bias current increases from 40 mAmp to 483 mAmp, suggesting an increase of the target sputtering rate.
Figure B-3. HC Ar flow rate is 9 SCCM and discharge current is 9.5 Amp (Neut. Bias current 10 Amp). Discharge voltage and target bias current change as a function of source Ar flow rate.

Figure B-2 shows that at a fixed ion source discharge current (9.5 Amp), the discharge voltage and target bias current also change as a function of the source Ar flow rate. Different from the ion source discharge power supply, the target bias power supply is set at the constant-voltage mode of operation and the total target bias current cannot exceed 500 mAmp. As shown in Figure B-2, in Region I, the source Ar flow rate is between 8 SCCM to 35 SCCM, the ion source voltage exceeds the set point (100Volts), and the discharge current and the target bias current is not stable. In this region, the target bias current is limited by the ion source. In Region II, when the source Ar is between 40 to 55 SCCM, the ion source current can be maintained stably at 9.5 SCCM, and the discharge voltage drops as the source Ar flow rate increases. Though
the ion source is stable in this region, the target bias current reaches its highest value (500 mAmp) which causes an instability at the target bias set point voltage (-800 Volts). In Region III, when the source Ar flow rate is greater than 60 SCCM, the target bias voltage is stable at -800 Volts. Further increasing the source Ar flow leads to a decrease of the discharge voltage and the target bias current. The result suggests that the source Ar flow rate should be maintained in Region III to operate the ion source and bias target stably. To reach the highest target bias current (highest sputtering rate), the source Ar should be the lowest value in the Region III (different ion source discharge current will have different value).

With fixed ion source parameters, the parameters of the biased target were also investigated. In this set of experiments, the HC Ar was fixed at 9 SCCM and source AR flow rate was 60 SCCM. The Neutralizer keeper current was 1.5 Amp, and ion sources charge current was 9.5 Amp whereas the discharge voltage was about 45 Volts.
Figure B-3. When pulse width is 1 µsec and pulse period is 100 µsec, the target bias current change as a function of negative target bias voltage.

As shown in Figure B-3, when the target bias voltage changes from 0 to -100 Volts, the target bias current increases quickly. When target bias voltage further increases from -100 V to -800 V, the target bias current increases linearly.

Figure B-4. Target bias current changes as a function of pulse period (frequency) when pulse width is fixed at 1 µsec.

Figure B-4 shows that when the pulse width is fixed at 1 µsec and the target bias voltage at -800 Volts, the target bias current change as a function of pulse period. When the pulse period is lower than 30 µsec, the target bias current does not change as the pulse period increases. Further increasing the pulse period leads to a decrease of the target bias current. This result indicates that a shorter pulse period (higher frequency) leads to higher target bias current, suggesting a higher target sputtering rate. However, due to the voltage overshoot when the
positive pulse is applied, the pulse period should not be too short in order to improve the film deposition controllability and repeatability.
Bibliography


Yao was born on October 17th, 1985 in Shanxi, China to Lianbo Jin and Yan Huo. Yao attended Hangzhou Dianzi University from 2003 to 2008. She earned a dual B.S. in Applied Physics and Accounting Science. She began an M.S. program in Southeastern Louisiana University within the department of Physics and Chemistry. Her M.S. research was conducted on purification and photophysical properties study of higher fullerenes isomers. Following the obtaining of her M.S. degree in 2010, she began a Ph.D. research program in Penn State University within the department of Engineering Science and Mechanics. She conducted her research on reactive sputter deposition of VO$_x$, NiO$_x$, and MoO$_x$ thin films for uncooled infrared imaging.