REACTIVE SPUTTERING OF MIXED-VALENT OXIDES: A ROUTE TO TAILORABLE OPTICAL ABSORPTION

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REACTIVE SPUTTERING OF MIXED-VALENT OXIDES: A ROUTE TO TAILORABLE OPTICAL ABSORPTION

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ABSTRACT

REACTIVE SPUTTERING OF MIXED-VALENT OXIDES: A ROUTE TO TAILORABLE OPTICAL ABSORPTION

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This work details two specific research thrusts exploring the deposition and characterization of mixed valent oxide systems. The first of these thrusts investigated the effect of the oxygen content, during reactive sputter deposition, on the optical, chemical, and structural properties of oxides of molybdenum, germanium, and rhenium. Exploration of the Mo-O system was conducted using a technique known as modulated pulse power magnetron sputtering (MPPMS), while the Ge-O and Re-O systems were deposited via direct current magnetron sputtering (DCMS). Films deposited under poisoned mode conditions were shown to be highly transparent with refractive index (n) values of $n_{550} = 1.60$ for GeO$_2$, and $n_{550} = 1.97$ for MoO$_3$, similar to values reported for bulk constituents. The Re-O system, unlike Ge-O and Mo-O, displayed a significantly high sensitivity to ambient moisture. Chemical analysis via XPS indicated the presence of
instability as a result of the moisture induced decomposition of Re$_2$O$_7$ into HReO$_4$, and catalytic disproportionation of Re$_2$O$_3$ into Re and hydrous ReO$_2$.

The second research thrust within this project was focused on the deposition of three component mixed oxide systems with multiple valence states. This effort, which utilized the results from individual material depositions mentioned previously, required the use of stable and thermodynamically compatible material systems, namely Mo-O and Ge-O ($\Delta f^0_{\text{H}_0}(\text{MoO}_2) = -588$ kJ/mol and $\Delta f^0_{\text{H}_0}(\text{GeO}_2) = -580$ kJ/mol). Note that Re-O was not explored as part of the ternary deposition effort due to the aforementioned chemical instability. To achieve the goal of depositing mixed valent thin films with tailorable optical absorption, an industrially scalable co-deposition method was devised in order to deposit molybdenum cations within a dielectric GeO$_2$ matrix. The high power densities associated with the MPPMS process were systematically varied in order to control the oxygen partial pressure via gettering, allowing for control over the oxidation state and concentration of Mo$^{4+}$ (MoO$_2$) and Mo$^{3+}$ (Mo$_2$O$_5$) cations within a transparent GeO$_2$ matrix. In addition, this work devised a modification to the Berg model for reactive sputtering that is capable of predicting the resulting oxidation states of Mo and Ge within a reasonable degree of accuracy. The co-deposition procedure devised within this work allowed for the optical gap of mixed Mo$_x$Ge$_y$O$_z$ films to be tailored between 3.4 eV and 0.4 eV, spanning useful ranges for devices operating in the visible and near-infrared.
To Mom, Dad, Shauna, Kristen, Jenna, and Jaime
ACKNOWLEDGEMENTS

As I complete this document, and my course of study at the University of Dayton, it has become extremely clear that none of this would have been possible without the guidance and support of a very large number of people. While it is impossible to list all of the names within this small section, I’d like to extend my most sincere gratitude to the following people…

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LIST OF ABBREVIATIONS AND NOTATIONS

MPPMS  modulated pulse power magnetron sputtering
HIPIMS  high power impulse magnetron sputtering
DCMS   direct current magnetron sputtering
OES    optical emission spectroscopy
iSE    in situ spectroscopic ellipsometry
SE     spectroscopic ellipsometry
n      real component of the refractive index
ñ      complex refractive index
k      imaginary component of the refractive index
UV     ultraviolet radiation
Vis    visible light
NIR    near infrared radiation
DRA    diffuse reflectance accessory
XRD    x-ray diffraction
GIXRD  grazing incidence x-ray diffraction
XRR    x-ray reflectivity
AFM    atomic force microscopy
XPS    x-ray photoelectron spectroscopy
Q_{p}  oxygen uptake by pumping system (sccm)
Q_{Ar} argon flow rate (sccm)
\( Q_{O_2} \) oxygen flow rate (sccm)
\( P_{O_2} \) oxygen partial pressure (Pa)
\( P_{Ar} \) argon partial pressure (Pa)
\( P_{TOT} \) total working pressure (Pa)
\( F \) reactive gas flux (atoms/m\(^2\)s)
\( k \) Boltzmann's constant, \( 1.3806488 \times 10^{-23} \) m\(^2\) kg s\(^{-2}\) K\(^{-1}\)
\( T \) Temperature (K)
\( m \) mass of reactive molecule (g/mol)
\( J \) current density (A/m\(^2\))
\( q \) electron charge, \( 1.60217657 \times 10^{-19} \) Coulombs
\( \alpha \) sticking coefficient
\( \theta_t \) target compound coverage fraction
\( Y_m \) sputter yield of elemental component of target surface
\( Y_c \) sputter yield of compound component of target surface
\( F_c \) compound flux (atoms/m\(^2\)s)
\( F_m \) metal, or elemental flux (atoms/m\(^2\)s)
\( A_t \) target area (m\(^2\))
\( A_c \) collector, or substrate area (m\(^2\))
\( Q_c \) oxygen uptake by compound formation on collector surfaces (sccm)
\( S \) pumping speed (L/s)
\( y \) target 1 surface fraction
\( V \) valence number
\( V_{max} \) maximum valence number
\( RF \) radio frequency
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<td>oxygen gas ratio</td>
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<td>RBS</td>
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<tr>
<td>Δ</td>
<td>change in phase of polarized light after interaction with film layer</td>
</tr>
<tr>
<td>d</td>
<td>film thickness (nm)</td>
</tr>
<tr>
<td>r</td>
<td>deposition rate (nm/min)</td>
</tr>
<tr>
<td>E_g</td>
<td>optical gap energy (eV)</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength (nm)</td>
</tr>
<tr>
<td>h</td>
<td>Planck’s constant, $6.62606957 \times 10^{-34}$ m$^2$ kg / s</td>
</tr>
<tr>
<td>ν</td>
<td>Frequency (Hz)</td>
</tr>
<tr>
<td>BE</td>
<td>electron binding energy (eV)</td>
</tr>
<tr>
<td>MOS</td>
<td>metal-oxide-semiconductor device</td>
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</table>
1. INTRODUCTION

Reactive physical vapor deposition has been used since the advent of thin film technology in order to obtain desired compounds from elemental precursors [1-4]. Specifically, the use of reactive deposition techniques allows for the fabrication of a variety of oxides, nitrides and carbides of metallic and semiconducting base materials [1-6]. In addition to the compounds made available through reactive techniques, there are also several routes of physical vapor deposition that have shown to be highly amenable with reactive processes. Such methods include: pulsed laser deposition, evaporative deposition techniques such as arc evaporation, thermal evaporation, electron beam evaporation, as well as plasma glow assisted processes including direct current, radio frequency, high power impulse, and modulated pulse power variants of magnetron sputtering. All of the aforementioned techniques can be used to grow high quality thin films under proper conditions, although, the use of magnetron sputtering techniques has provided a readily scalable, stable method for growing highly uniform compound thin films from elemental precursors. Reactive magnetron sputtering for the growth of thin oxide films has been particularly promising due to its ability to deposit dense oxide coatings with minimal surface roughness and high deposition rates [7-11]. The high densities and deposition rates of oxide thin films have shown to be quite valuable within the optical coatings industry. While transparent oxides have been the backbone of optical coating design since its inception in the early 19th century [12-14], recent works
exploring sub-stoichiometric oxide systems have generated interest due to their unique absorptive properties [15-17]. Specifically, the systematic variation of oxygen content within multi-component inorganic oxides has shown promise for obtaining thin films with absorption features spanning visible and infrared wavelengths [15-17]. Mixed-valent oxide films are of interest in several applications including solar collectors, absorbing anti-reflective coatings, decorative glasses, transparent-conductive coatings, and electrically switchable “smart-windows”.

This work explores the fabrication and characterization of oxides of germanium (GeO\(_x\) (0<x\(\leq\)2)), molybdenum (MoO\(_x\) (0<x\(\leq\)3)), and rhenium (Re\(_x\)O\(_y\) (0<x\(\leq\)2, 0<y\(\leq\)7)), thin films to obtain a variety of optical properties through variation of oxygen partial pressure during growth. Individual characterization of these material systems allows for a proper understanding of their specific properties, and feasibility of deposition. Thus, this project will first explore synthesis of the individual material systems, determine the environmental stability of Re\(_x\)O\(_y\) thin films, and finally, develop a method for the co-deposition of mixed Mo\(_x\)Ge\(_y\)O\(_z\) thin films. GeO\(_2\) and MoO\(_3\) were chosen for several reasons, first being their multitude of applications listed within section 1.2, second being the similarities in their respective enthalpies of formation at room temperature. The enthalpy of formation governs the thermodynamic driving force for reactivity; thus, a highly negative enthalpy of formation results in a strong likelihood of oxide formation at given temperatures and oxygen partial pressures. The Ge-O and Mo-O systems are of interest due to the fact that the enthalpies of formation of substoichiometric MoO\(_2\) (relative to MoO\(_3\)) and stoichiometric GeO\(_2\) are very similar at room temperature, \(\Delta_fH^0_{\text{(MoO}_2\text{)}} = -588\text{ kJ/mol}\) and \(\Delta_fH^0_{\text{(GeO}_2\text{)}} = -580\text{ kJ/mol}\) [18], a potential indicator that
these two compounds can be deposited concurrently. Therefore, it should be possible to control the amount of absorptive, substoichiometric MoOₓ (0<x<3) compounds within a transparent, dielectric GeO₂ matrix.

This work had four primary goals. The first (i) was to obtain an understanding of the effects of oxygen concentration on the optical, chemical, and structural properties of reactively sputtered GeOₓ, ReₓOᵧ, and MoOₓ thin films. For the analysis of the GeOₓ and ReₓOᵧ material systems, films were deposited using reactive DC magnetron sputtering at oxygen levels corresponding to the growth of elemental films, mixed composition sub-oxides and finally, stoichiometric GeO₂ and mixed valent ReO₃. A similar approach was used for the growth of MoOₓ, except a technique known as modulated pulse power magnetron sputtering (MPPMS) was utilized in place of traditional DC magnetron sputtering (DCMS). The MPPMS approach was used for the MoOₓ system due to its ability to provide peak target power densities in excess of 500 W/cm² [4,19,20], allowing for rapid depletion of oxide buildup on the surface of the sputtering target and minimizing process hysteresis [4,19,21-25]. The MPPMS power supply is also capable of automated arc suppression, reducing the occurrence of spurious droplets released by arcing during reactive sputtering [4,19,21-25].

Second (ii), this project sought to establish a reliable method of deposition for mixed-valent rhenium oxide thin films. Characterization of rhenium oxide films assessed the effects of deposition conditions on the optical, structural, and chemical properties of these films. In addition, further characterization after specified periods of atmospheric exposure were conducted in order to establish whether or not these thin films would be robust enough for use within optical devices. This material was explored in depth due to
its unique absorption characteristics throughout visible and near-infrared wavelengths, as well as its potential as a replacement for silver within multilayer optical devices [26-29].

The third goal (iii) of this project was to determine the feasibility of developing a unique, scalable method for depositing mixed Mo$_x$Ge$_y$O$_z$ thin films via co-deposition of individual elemental constituents. Development and optimization of the co-sputtering procedure, using DCMS and MPPMS techniques, was performed using a combination of empirical and model-based data.

Finally (iv), this work sought to conduct comprehensive characterization of films deposited within the Mo-Ge-O system in order to elucidate the reduction pathway for GeO$_2$ and MoO$_3$ as a function of residual oxygen content within the chamber. Detailed understanding of the reduction behavior of each material, as a function of processing conditions, has allowed for the systematic tailoring of both the physical, optical, and chemical properties of the deposited films. In addition, a phenomenological process model was constructed in order to analyze the relationship between oxygen partial pressure and the resulting valence states of components within the films.

This project utilized many disparate materials, such as dielectric oxides (MoO$_3$, GeO$_2$), conductive oxides (ReO$_3$), and mixed substoichiometric oxides (Mo$_x$Ge$_y$O$_z$). Optimization and control over reactive sputtering of each of these materials has allowed for increased understanding and manipulation of their unique properties, working towards the ultimate goal of depositing materials with engineered optical absorption.
1.1 Background

A large amount of attention has been devoted to thin film oxide materials, including group V-VII transition metal oxides and oxides of semiconductors. The former group, the transition metal oxides, contains a large variety of elements with a wide variety of uses. Such applications include, but are not limited to: chemical sensors [30-35], optically switchable “smart windows” [36,37], diffusion barrier interlayers, high refractive index (n) coatings within multilayer interference filters [38,39], and catalytic applications [40-44]. One family of transition metal oxides that has garnered significant attention are oxides of group VI elements, including chromium trioxide (CrO$_3$), molybdenum trioxide (MoO$_3$) and tungsten trioxide (WO$_3$). The first, CrO$_3$, is typically used for hard coatings and anti-corrosion applications due to its ability to facilitate passivation. However, the toxicity of the hexavalent state, Cr$^{6+}$, has precluded it from more widespread usage [45,46]. MoO$_3$ and WO$_3$, on the other hand, have been shown to be useful for applications in electronics [36,44,47-53], catalysis [40-44], and optical thin film coatings [17,38,39,54]. In their crystalline forms, metastable β-MoO$_3$ and WO$_3$ are known as defect perovskites, consisting of a network of corner-sharing MO$_6$ (M-Metal) octahedra. The structures resulting from these octahedra give rise to tunnel-like structures that can accommodate interstitial impurities [29]. Note, these materials are commonly called defect perovskites, or perovskite-type, due to the lack of the body-centered atom present in traditional perovskite materials such as BaTiO$_3$ [29].

One characteristic that has led to a large amount of interest in MoO$_3$ and WO$_3$ is their ability to facilitate changes in band structure and optical absorption through ion intercalation, oxidation, and reduction [55,56]. Permanent changes in coloration,
involving the facile manipulation of the oxidation state, are typically brought on by heating the materials in reducing or oxidizing environments. Reversible changes in band structure and coloration brought on by ion intercalation are described by the suffix “-chromism”, while changes brought on by the manipulation of the oxidation state are described using the suffix “-coloration” [55,56]. Chromism can be achieved with MoO₃ and WO₃ through ion intercalation brought on by UV irradiation (photochromism), charge injection (electrochromism), gaseous diffusion (gasochromism), and thermal excitation (thermochromism) [36,44]. WO₃ and MoO₃ are transparent due to the sufficiently large energy gap (2.6-3.4 eV) between their t₂g and p× bands, becoming opaque upon the insertion of singly charged metallic ions, typically H⁺, Li⁺, Na⁺, or K⁺ [29]. Once a sufficiently large fraction of metallic ions are intercalated within MoO₃ or WO₃, their excess electrons occupy the previously unfilled t₂g band, causing a reversible loss of transparency [29]. Exploration of perovskite-type oxides for use in electro- and gasochromic “smart windows” that are able to selectively transmit or absorb and reflect light has led to a large amount of interest within the past decade. In addition to chromic effects, the ease in manipulation of the valence state of Mo and W oxides allows for the ability to readily exchange lattice oxygen atoms with external compounds. This variability in oxidation results in a low degree of thermal stability, leading to sublimation at 795 ºC for MoO₃ and 1473 ºC for WO₃ [18], rendering them unusable for ultra high temperature applications. Since MoO₃ is significantly less thermally stable than WO₃, its ease of dissociation may prove valuable for applications requiring substoichiometric components.
While the instability of MoO$_3$ and WO$_3$ precludes them from use as refractory components, it affords them a large amount of usefulness as catalysts for the reduction and oxidation of various hydrocarbon species [40-44]. Additionally, the ease of manipulating the oxidation states of WO$_x$ and MoO$_x$ allows for applications in chemical sensing [36,44,57-59]. Finally, WO$_3$ and MoO$_3$ both demonstrate similarly high refractive indices, 2.0-2.2 [15,56,60], and transparency throughout visible wavelengths (400-750 nm), making them useful as high index layers in dielectric interference filters [38,39].

Like WO$_3$ and MoO$_3$, the transition metal oxide ReO$_3$ is also a “defect perovskite” consisting of a network of corner sharing ReO$_6$ octahedra in its crystalline form [26,27]. This crystal structure, shared by ReO$_3$, MoO$_3$, and WO$_3$ is also called the “Rhenium Oxide” structure [29]. Being a part of the group VII elements, rhenium has one more outer-shell electron than molybdenum and tungsten. This additional electron resides between the t$_{2g}$ and p$_{\pi}$ bands, within the 5d shell, causing the material to be absorptive in its oxidized form [26-29]. The presence of a lone electron within the lower portion of the 5d shell, similar to silver, accounts for the high electrical conductivity of ReO$_3$, $\sigma_{\text{ReO}_3}=10^3$-$10^4$ (Ω cm)$^{-1}$ [28,61], as well as its unique absorption features within visible and near-infrared wavelengths. Like silver, ReO$_3$ is conductive, but has a lower extinction coefficient throughout visible wavelengths, and is able to effectively absorb near infrared wavelengths. Thin films of ReO$_3$ have been used for many applications, including catalysis [62-66], interfacial layers for high temperature superconductors [61], buffer layers for polymer solar cells [67], and electrical contacts for liquid crystal devices.
Despite concerns pertaining to the environmental stability of ReO$_3$, its unique optical and electrical behavior makes it a promising candidate for further investigation.

Additional materials that are not encompassed within the transition metal category include oxides of germanium and silicon. Both germanium and silicon form thermally stable oxides, with approximate melting temperatures of 1100ºC and 1700ºC [18], respectively. In addition to their high thermal stability, these materials have found a large variety of uses ranging from telecommunications to architectural glass. Silicon, specifically, has been extremely well characterized as the chief component within nearly all modern glasses, low index layers within multilayer dielectric interference coatings [38,39], and diffusion barriers in electronics. Similarly, germanium oxide has been used as a high index layer to coat SiO$_2$ fibers for optical communication, due to its slightly higher refractive index $n=1.60$ versus $n=1.47$ for SiO$_2$ [18]. In addition to use in telecommunication, germanium oxide layers can also be used within dielectric interference filters [8,10,68], as a dopant in silica glass [69,70], and as a dielectric interlayer for electronic devices [71-73]. It is worth noting that both silicon oxide and germanium oxide have highly negative enthalpies of formation, $H_f^{\circ}$(SiO$_2$) = -901 kJ/mol and $H_f^{\circ}$(GeO$_2$) = -580 kJ/mol, making them likely to form compounds upon exposure to oxygen. While both SiO$_2$ and GeO$_2$ have been researched extensively, especially SiO$_2$, there are several opportunities for novel research concerning in-situ growth monitoring, characterization of substoichiometric compounds, and deposition of novel mixed-oxide thin films. Recently, sub-oxides of germanium (GeO$_{2-x}$) have been explored in depth due to their tendency to form passivating inter-layers within metal-oxide-semiconductor
A new area of research that has been attracting interest employs magnetron sputtering techniques to obtain mixtures of various semiconductor and transition metal oxides. Specifically, studies by Gil-Rostra et al. [15] have utilized reactive magnetron sputtering to tailor the absorption of substoichiometric transition metal sub-oxides within a dielectric silicon dioxide matrix. Oxide systems explored include Cr, Fe, Cu, W, and Mo. Gil-Rostra et al. were able to deposit colorful thin film coatings utilizing the same materials that have been employed by glass blowers and ceramists for centuries in the creating of “ionic-glasses” by depositing absorptive metallic ions within a dielectric matrix. Thin films capable of visible light absorption have found uses in decorative coatings, light attenuating layers within Bragg-reflectors, and selective absorbers for solar collectors, to name a few. The magnitude of absorption can be controlled by varying the fraction of absorptive metallic ions within the dielectric matrix. The absorption characteristics, and subsequent coloration, of specific ionic compounds are influenced by their long range (crystalline), short range order (molecular), and the subsequent band structure of the material [15]. Band structure plays an important role in determining the onset of absorption features attributed to band-to-band transitions, or transitions from the valence band to the conduction band. Additional absorption effects can be brought on by insertion effects due to the presence of electrons within the conduction band. The utilization of magnetron sputtering for deposition of selectively absorbing ionic glasses is highly promising due to its ability to fabricate dense, smooth coatings with a high degree of repeatability.
2. EXPERIMENTAL PROCEDURES

2.1 Thin film deposition

A load-locked, 195 liter stainless steel high vacuum chamber was used to deposit, and aid in the investigation of the optical, chemical, and physical properties of GeO$_x$, MoO$_x$, Re$_x$O$_y$, and Mo$_x$Ge$_y$O$_z$ thin films. The chamber used for these experiments (Figure 1) was evacuated to a base pressure of $8.0 \times 10^{-5}$ Pa ($6.0 \times 10^{-7}$ Torr), or better, using a turbomolecular pump with a maximum effective pumping speed of 350 L/s [78].

![Diagram of magnetron sputter chamber and sample introduction chamber.](image)

Figure 1. Schematic of magnetron sputter chamber and sample introduction chamber.

Substrates, consisting of $\alpha$-quartz (Machine Glass Inc.) and p-type (100) silicon (University Wafer LLC) were loaded into the deposition chamber via the transfer arm in
the introduction chamber after pumping to a base pressure of 1.0x10\(^{-4}\) Torr via turbomolecular pumping. The source materials used, also known as targets or cathodes, were elemental Ge (99.999% purity, Plasmaterials), Mo (99.99%, K.J. Lesker), and Re (99.99%, K.J. Lesker). The levels of the reactive gas, oxygen (99.995% purity), and inert gas, argon (99.999%), within the chamber were controlled through separate mass flow controllers (MKS and ALICAT). The total reactive and inert gas pressure (\(P_{TOT}\)) within the deposition chamber was controlled using an automated gate valve assembly capable of varying the pumping speed (\(S\)) via adjustment of conductance. For individual material deposition, a \(P_{TOT}\) of 1.33 Pa (10 mTorr) was used, while the fractions of oxygen and argon were varied systematically. For co-deposition, a constant pumping speed was set to obtain an argon pressure (\(P_{Ar}\)) of 1.33 Pa (10 mTorr) prior to the addition of oxygen. Subsequently, the introduction of oxygen at a constant pumping speed, in addition to a known argon partial pressure, allows for the determination of the respective oxygen uptake, or “gettering”, during the simultaneous Mo-O and Ge-O depositions. \(P_{TOT}\) was measured using a capacitance manometer. All materials, except for GeO\(_x\), were grown at a temperature of 25 °C, with no external heating applied outside of thermal contributions from the deposition flux. GeO\(_x\) thin films were grown at 100 °C, including thermal contributions from the plasma. The deposition chamber can be equipped with up to four unbalanced, 50 mm magnetron sources. All magnetron sources are set within a confocal arrangement [1] at an incidence angle of 20° with respect to the substrate surface normal. 50 mm magnetron guns manufactured by both K.J. Lesker Co. (Torus) and Meivac (MAK) were utilized for all depositions. Plasma generation took place using either an Advanced Energy MDX DC power supply or a ZPulser Axia modulated pulse power
supply. For depositions of GeO\textsubscript{x}, MoO\textsubscript{x}, and Re\textsubscript{2}O\textsubscript{y}, all other guns were retracted to mitigate distortion of the magnetic field of the active magnetron, placed at a distance of 9 cm from the substrate surface. For co-deposition of Mo\textsubscript{y}Ge\textsubscript{z}O\textsubscript{w}, two diametrically opposed magnetrons were used at a working distance of 13 cm. For depositions requiring two magnetrons, the magnets within one of the guns were flipped to ensure opposite polarity, providing a closed magnetic field as shown in Figure 2a [1]. All specimens were rotated in-plane to ensure radial uniformity.

![DUAL MAGNETRON](image)

Figure 2. Photograph of (a) closed magnetic field and (b) mirror magnetic field configurations. From Musil 2005 [1], used with permission from Elsevier Limited.

2.2 Plasma characterization

Time averaged optical emission spectroscopy (OES) allowed for qualitative analysis of the relative intensity of Ar, O\textsubscript{2}, Ge, Mo, and Re photoemission events within the plasma discharge. Optical emission generated during the deposition process was collected by an external fiber optic placed directly before a quartz viewport 45 cm from the plume. Spectra were processed with an OceanOptics USB 4000 spectrometer using an integration time 500 ms and dark correction to reduce the effects of ambient light prior to plasma ignition.
2.3 Optical characterization

*In-situ* spectroscopic ellipsometry (iSE) was used to provide real-time information pertaining to the optical properties of the growing thin film. The iSE system, a J.A. Woollam co. M2000VI, consists of a detector and broadband (380-1700 nm), polarized, white light source mounted to opposing sides of the chamber, resulting in an angle of incidence of 70° with respect to the sample surface normal. The thickness, and complex refractive index, \( \tilde{n} = n + ik \), where \( n \) is the real part of the refractive index and \( k \) comprises the imaginary portion, are interrogated through analysis of the change in polarization experienced by linearly polarized light after interaction with the sample surface [79]. Data acquisition times were set at an integer multiple of the rotation period to ensure a consistent sampling area. *Ex-situ* measurements were performed using the same M2000VI system after venting the chamber. All data processing was performed using the CompleteEASE v. 4.7 software package.

A Varian Cary 5000 ultraviolet (UV)-visible (Vis)-near infrared (NIR) spectrophotometer was used to obtain transmission and reflectance spectra for wavelengths ranging from 250-2500 nm. Specular and diffuse reflectance components were measured using a diffuse reflectance accessory (DRA). Reflectance and transmission measurements were used to calculate the optical absorption coefficient, \( \alpha \), for validation of ellipsometry measurements and calculations [80].

2.4 Structural and morphological characterization

Physical properties of the thin films were probed using a multi-tiered approach to provide measurements of density, surface morphology, and to determine any presence of
long-range crystalline order. A Rigaku Smart-Lab x-ray diffractometer (XRD) was used to provide measurements of crystallinity via grazing incidence angle 2θ-ω scans (GIXRD), where the detector angle (ω) was set at 0.35° to ensure minimal substrate diffraction. x-ray reflectivity (XRR) was used to calculate density, roughness, and thickness by analyzing the diffraction and attenuation behavior of x-rays at very small angles (0.002-5°). GIXRD and XRR measurements were performed using Cu-Kα (λ=0.154180 nm) x-rays. Additional analysis of the surface morphology, namely roughness, was conducted using a Nanoscope V atomic force microscope (AFM). Roughness measurements were conducted using tapping mode, with a laser measuring the deflection of a cantilever tip as it rasters across the surface of the sample. Surface roughness measurements obtained by AFM are used to corroborate roughness values measured by XRR analysis. Rigaku GlobalFit software was employed for all XRR data analysis and processing.

2.5 Chemical analysis

Surface analysis via x-ray photoelectron spectroscopy (XPS) was employed in order to analyze the composition and chemistry of the films. Scans were collected using a Physical Electronics (PHI) 5700 XPS as the primary analysis instrument. A Kratos AXIS Ultra XPS and a Surface Science Instruments’ M-Probe, were also used based on availability and sample geometry considerations. All XPS instruments used are equipped with several x-ray sources capable of generating monochromatic aluminum Kα x-rays (1486.7 eV), silver Lα x-rays (2984.2 eV), and magnesium Kα x-rays (1254.6 eV) [18]. Unless otherwise noted, XPS data within this work was obtained using monochromated aluminum Kα x-rays. Survey scans in the PHI XPS were taken at an analyzer pass energy
of 187.85 eV, while high resolution scans mostly used a pass energy of 29.35 eV. Survey scans were taken for binding energies from 0 to 1400 eV, while binding energy ranges for high energy resolution scans, scanning relevant core level electron transitions, were chosen based on the chemical species present in the films. For convenience, spectra were energy calibrated with respect to the adventitious carbon 1s transition at a binding energy of 284.6 eV, unless otherwise noted [81]. In certain cases, calibration was forgone in order to preserve the fidelity of the raw data. Fitting of the XPS spectra employed the CasaXPS 2.3.16 software package [82]. Parameters including full width at half maximum peak height, location of peak center and peak area were determined after using a Shirley background subtraction. A mixed Gaussian-Lorentzian line shape was used for the peak fitting.

2.6 Modeling of reactive processes

Given the complex, non-linear behavior associated with the reactive co-sputtering process, a model-based approach was required to de-couple the effects of main process variable, \( U_c \), on the response of the individual Ge and Mo targets. Parameters analyzed through modeling include the change in oxygen partial pressure (\( P_{O2} \)) as a function of total oxygen flow rate (\( Q_{TOT} \)), as well as providing estimation of the valence state of each constituent element present. The analysis of \( P_{O2} \) and the resulting valence states of the film provides a direct relationship between the amount of oxygen available for compound formation and the specific coordination compounds formed. The use of process modeling is especially important when operating two targets simultaneously, as is the case for the deposition of \( \text{Mo}_x\text{Ge}_y\text{O}_z \) thin films within chapter 6. The modeling approach used within chapter 6 employs a variant of the “Berg” model, developed by S. Berg and T. Nyberg,
which has been adapted for the co-sputtering process [83,84]. The model was constructed within the MATLAB r2010b software package, wherein a graphical user interface (GUI) was also created in order to provide ease in calculation and adaptability for use in a laboratory environment. The GUI, sputter yield calculations, and the associated MATLAB script are shown in Appendices A-C.

While the Berg model is described in-depth elsewhere [83,84], this section contains a brief overview of its basic principles, as well as the additions made to it within this work. The Berg model requires a chamber setup that allows for control over the pumping speed (S), total oxygen flow rate ($Q_{TOT}$), and inert gas flow rate ($Q_{Ar}$). A schematic of the basic chamber setup is shown in Figure 3.

![Figure 3. Schematic of a simple reactive sputtering chamber, from [83], used with permission from Elsevier Limited.](image)

Measurement of the oxygen partial pressure ($P_{O2}$) can be achieved through the addition of oxygen while $S$ and $Q_{Ar}$ remain constant. Once the argon pressure ($P_{Ar}$)
achieves steady-state, oxygen can be introduced into the chamber where the total pressure (\(P_{\text{TOT}}\)) is now equivalent to the sum of \(P_{\text{Ar}}\) and \(P_{\text{O}_2}\). Since oxygen is continually used up through compound formation with deposited material, also known as chemisorption, \(P_{\text{O}_2}\) will continually change based on the deposition conditions during sputtering. \(P_{\text{Ar}}\) is expected to remain constant due to the inert nature of argon. Measurement of \(P_{\text{O}_2}\) allows for the calculation of the oxygen flux (\(F=\text{oxygen molecules/unit area/unit time}\)) that all of the surfaces of the chamber, including the targets and substrate, are exposed to. \(F\) can be calculated using the following equation. Note that \(k\) is Boltzmann’s constant, \(T\) is the temperature (K), and \(m\) is the mass of the \(O_2\) molecule (32 g/mol).

\[
F = \frac{P_{\text{O}_2}}{\sqrt{2kT\pi m}}
\]  

(1)

Now that the conditions for calculating \(F\) have been determined, the next important parameter describes the fraction of the target surface that has been oxidized (\(\theta_t\)). One of the main assumptions used by Berg et al. states [83],

“The only way sputtered compound molecules may be replaced is by reactions between neutral reactive gas molecules and the elemental non-reacted target material.”

The previous statement is described in mathematical form by Equation 2, allowing for

\[
\frac{I}{q} Y_c \theta_t = \alpha 2 F(1-\theta_t)
\]

(2)

the calculation of \(\theta_t\). Parameters required for calculating \(\theta_t\) include the sputter yield of the compound material (\(Y=\text{ejected atoms/ion impact}\)), the current density (A/m\(^2\)) experienced at the cathode (\(J\)), the principal electron charge (\(q\)), and the sticking coefficient (\(\alpha\)). \(J\) values based on electron current density are used in the Berg model to estimate the
number of Ar\(^+\) impacts on the surface of the target. Additionally, the sputter yields of the elemental (Y\(_m\)) and compound (Y\(_c\)) atoms are calculated as a function of applied voltage using the SRIM/TRIM 2013 software package (Table 1) [85]. All default parameters values are shown in Appendix A.

Table 1. Sputter yields calculated with the SRIM/TRIM 2013 software package [85].

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<th>I</th>
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<th>O</th>
<th>Mo (O N(_2))</th>
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<th>I</th>
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<td>0.13</td>
<td>0.51</td>
<td>1.03</td>
<td>0.70</td>
<td>513</td>
<td>0.19</td>
<td>0.45</td>
<td>1.35</td>
<td>1.39</td>
<td>1.35</td>
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<tr>
<td>370</td>
<td>302</td>
<td>1.20</td>
<td>0.14</td>
<td>0.55</td>
<td>1.11</td>
<td>0.74</td>
<td>513</td>
<td>0.19</td>
<td>0.45</td>
<td>1.35</td>
<td>1.39</td>
<td>1.35</td>
</tr>
<tr>
<td>375</td>
<td>323</td>
<td>1.47</td>
<td>0.14</td>
<td>0.55</td>
<td>1.17</td>
<td>0.77</td>
<td>511</td>
<td>0.19</td>
<td>0.45</td>
<td>1.35</td>
<td>1.37</td>
<td>1.35</td>
</tr>
<tr>
<td>380</td>
<td>372</td>
<td>2.67</td>
<td>0.16</td>
<td>0.64</td>
<td>1.30</td>
<td>0.86</td>
<td>506</td>
<td>0.19</td>
<td>0.43</td>
<td>1.29</td>
<td>1.37</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Once \(\theta_t\) is determined, it is possible to calculate the deposition flux of both compound (\(F_c\)) and elemental atoms (\(F_m\)). \(A_t\) and \(A_c\) represents the area of the target and substrate in m\(^2\).

\[
F_c = \frac{J}{q} Y_c (\theta_t) A_t
\]

\[
F_m = \frac{J}{q} Y_m (1-\theta_t) A_t
\]

Equations 3 & 4 allow for the user to determine the composition of the deposition flux.

Furthermore, solving for the parameters within Equations 1-4 allows for the calculation of the net oxygen uptake due to compound formation upon the surface of the target (\(Q_t\)). The total reactive gas flow rate (\(Q_{TOT}\)) is a user defined parameter, as described by Equations 5-8.
In the above equations, \( Q_t \), \( Q_c \), and \( Q_p \) represent oxygen uptake (sccm) attributed to chemisorption on the target and substrate surfaces, and pumping, respectively. Additionally, \( S \) represents the pumping speed (L/s), \( \theta_c \) is the compound surface fraction on the substrate, and \( A_c \) is the area of the substrate. Calculation of \( \theta_c \) is important due to the fact that it is directly related to the film chemistry. It is possible to solve for \( \theta_c \) using Equations 1-5. The relationship among the key parameters in the Berg model is depicted schematically in Figure 4. Since the specific application of the modeling within this work requires the use of two targets, the single target system shown in Figure 4 must be modified in order to establish key variables for each target and collecting surface. In the two-target Berg model, variables associated with target 1 material are assigned a subscript of 1, \( et cetera. \) Additionally, the substrate is further subdivided by assigning the portion of its surface area that is coated with target 1 compound material, as \( y \), shown in Figure 5.
Figure 4. (a) Visualization of the parameters described within the Berg model. (b) Illustration of the flux distribution related to compound formation on the target and substrate, from [83], used with permission from Elsevier Limited.

Figure 5. Schematic of the variables present within the two-target Berg model, from [83], used with permission from Elsevier Limited.
The original Berg model was modified within this work in order to calculate the valence state of the deposited films. Valence state calculations were performed using a stepwise relationship based upon empirical XPS chemical state data. Processing conditions related to the growth of fully stoichiometric compounds were considered to be within the “poisoned regime”, while the formation of mixed-valent oxide compounds was assumed to signify the onset of transition mode sputtering. As such, depositions within the poisoned mode signify excess oxygen, indicative of a $\theta_t$ approaching 1. Since $\theta_c > \theta_t$ due to the additional oxygen flux incident to the substrate surface, it can be assumed that the substrate will also be fully oxidized [83]. The valence state ($V$) attributed to poisoned mode sputtering is shown in Equation 9. Note that $V_{\text{max}}$ is the maximum valence state of the target material.

$$V = V_{\text{max}} \theta_c$$  \hspace{1cm} (9)

In the case of transition mode sputtering, calculation of the valence state becomes more difficult due to the large decrease in $P_{O_2}$. Therefore, the changes in $P_{O_2}$ must be taken into account when calculating the valence state. To accomplish accurate valence state estimation within the transition regime, a rule of mixtures approach was used, based on the magnitude of $P_{O_2}$, $\theta_c$ and $\theta_t$, as shown in Equation 10.

$$V = N_p \left[ \theta_c \left( \frac{P_{O_2}}{P_{O_2 \text{max}}} \right) + \theta_t \left( 1 - \frac{P_{O_2}}{P_{O_2 \text{max}}} \right) \right]$$  \hspace{1cm} (10)
3. DEPOSITION AND CHARACTERIZATION OF DC SPUTTERED GERMANIUM OXIDE (GeO\textsubscript{x}) FILMS

3.1 Introduction

Germanium dioxide (GeO\textsubscript{2}) is a versatile, wide band gap material that has been explored in depth due to its promising thermal, optical, and electrical properties. Specifically, GeO\textsubscript{2} is thermally stable, has a high dielectric constant, and exhibits a refractive index that is slightly higher than that of SiO\textsubscript{2} [7,71,77,86-90]. Applications of GeO\textsubscript{2} thin films include usage in optical waveguides [71,86,87,91,92], dielectric layers in capacitors [71-73], microbolometers [93], and optical filter elements [8,10,68]. In addition, sub-stoichiometric GeO\textsubscript{2}, or GeO\textsubscript{x}, has been studied in depth due to its tendency to form a passivating inter-layer within Ge-based metal-oxide-semiconductor (MOS) devices [74,75], and for its potential in electronic memory storage devices [76,77].

Several methods of depositing GeO\textsubscript{2} films have been explored previously, including radio frequency (RF) magnetron sputtering [71,72,86,87,90,93-96], laser ablation [8], sol-gel deposition [77,91,92], reactive thermal evaporation [68,73,97], e-beam evaporation [98], plasma enhanced chemical vapor deposition (PECVD) [99], and reactive DC magnetron sputtering [7-11]. Previous works performing in-depth analyses on the chemical, optical and electrical properties of GeO\textsubscript{2} films were conducted using films with thicknesses ranging from roughly 300 nm to 1.4 μm. Exceptions include experiments by Krupanidhi et al., measuring the electrical properties of 100 nm thick, e-
beam deposited GeO$_2$ [98], as well as electrical characterization of 3 nm thick GeO$_2$ interfacial layers by Murad et al. [73]. Lange et al. and Vega et al. have performed studies concerning the deposition and characterization of GeO$_x$ (0>$x$>2) films deposited by DC magnetron sputtering. Analyses conducted by Lange et al. have probed the optical and structural properties of GeO$_x$ thin films [7], while studies by Vega et al. were mainly focused on optical characterization [8].

The present work focuses on performing comprehensive optical, chemical and structural characterization of GeO$_x$ (0>$x$>2) films, approximately 100 nm thick, grown by DC magnetron sputter-deposition on single crystal (100), n-type silicon wafers. Studies were made to understand the effect of the oxygen gas fraction on the deposition rate, structure, chemistry, and optical constants of these very thin GeO$_x$ films. The results obtained are presented and discussed in this section.

3.2 Experimental

3.2.1 Fabrication

Germanium oxide (GeO$_x$) thin films were deposited within the stainless steel vacuum chamber described in section 2.1. After reaching the required pressure, research grade O$_2$ (99.995%) and Ar (99.999%) were introduced into the chamber through separate mass flow controllers. The working pressure, controlled via an automated gate valve assembly, was maintained at 0.67 Pa (5 mTorr). The O$_2$ flow rate was varied between 0.0 and 20.0 sccm at increments of 5.0 sccm, and the argon flow rate was adjusted to keep the net flow rate constant at 20.0 sccm. This means that the oxygen gas fraction ($\Gamma$), which is defined as the ratio of the O$_2$ gas flow rate ($Q_{O2}$) to the total (O$_2$+Ar) flow rate, was varied from 0.00 to 1.00 in order to understand its effect on the
deposition rate, structure, chemistry, and optical properties of the resulting films. The plasma was generated using an Advanced Energy MDX power supply at a power of 50 W DC. A shutter was used to shield the substrate from any spurious droplets caused by arcing at the onset of plasma ignition. The shutter was opened upon achieving a steady-state plasma. A 50 mm germanium sputter target (Plasmaterials, 99.999% purity), attached to a Meivac MAK magnetron sputtering gun, was used as the source material. All films were deposited on prime grade, n-type (100) Si wafers (University Wafer LLC). Wafers were placed on a rotating sample holder (8 rpm) located at a distance of 9 cm from the surface of the sputtering target. The substrate temperature was held constant at 100 ºC throughout all depositions.

3.3 Characterization

GeOₓ films were characterized by performing structural, chemical and optical measurements. Grazing incidence X-ray diffraction (GIXRD) and X-ray reflectivity (XRR) measurements were obtained using a Rigaku SmartLab X-ray diffractometer. The GIXRD and XRR measurements were made using Cu Kα radiation at room temperature.

Ion beam analysis of the GeOₓ films was performed in order to determine the chemical composition, thickness and elemental depth distribution. Rutherford backscattering spectrometry (RBS) experiments were carried out in the accelerator facility at the Environmental Molecular Sciences Laboratory (EMSL), at the Pacific Northwest National Laboratory (PNNL). The RBS experiments were performed at the National Electrostatic Corporation (NEC) RC43 end station. A 2 MeV He⁺ ion beam with a 7° angle of incidence measured from the sample normal was used. The backscattered
ions were collected using a silicon barrier detector at a scattering angle of 150°. Composition profiles were determined by comparing SIMNRA [100] computer simulations with the experimental data. The detailed procedure on using this simulation to obtain the stoichiometry and atomic concentration of the films has been discussed elsewhere [101]. In addition to RBS measurements, the chemical valence states of elements, and subsequent stoichiometries, within the films were analyzed using x-ray photoelectron spectroscopy (XPS). Most of the XPS measurements were made in a Kratos AXIS Ultra XPS, but a Surface Science Instruments’ M-Probe and a Physical Electronics 5700 were used for inert gas sputtering measurements on the films (the ion gun on the Kratos instrument was not operational). All of these instruments are equipped with sources capable of generating monochromatic Al-Kα (1486.6 eV) x-rays, silver La x-rays (2984.2 eV), and magnesium Kα (1254.6 eV) x-rays. Unless otherwise noted, Al-Kα x-rays were used to generate the spectra from all samples. Survey scans were obtained with a high analyzer pass-energy, while high energy resolution spectra, to study the chemical states of Ge, were obtained with a low analyzer pass energy. All high energy resolution spectra were fit using Gaussian-Lorentzian lineshapes, following Shirley background subtraction.

The optical properties of GeO₂ films were evaluated using spectroscopic ellipsometry (SE). Raw data was captured using a J.A. Woollam M2000V1 spectroscopic ellipsometer capable of measuring the magnitude (ψ) and phase difference (Δ) of polarized light after interaction with the specimen. Data was processed within the CompleteEASE v. 4.7 software package. Raw data was fit with a Cauchy oscillator model in order to estimate the refractive index, extinction coefficient, and thickness (d).
However, films with low oxygen content were fit using a general oscillator model with two Tauc-Lorentz oscillators, accounting for the free-carrier absorption associated with amorphous germanium.

3.4 Results and discussion

3.4.1 Deposition rate

The film thickness was determined by three independent methods, SE, XRR and RBS, and was divided by the respective deposition time in order to determine the deposition rate for the various oxygen gas fractions. In addition to thickness determination, XRR was also used to measure the density of the GeO\textsubscript{x} films. Figure 6 illustrates the density of the GeO\textsubscript{x} films as a function of Γ. Note the good quality of fit between the model calculations and the measured data shown in Figure 7. The variation of deposition rate with Γ is shown in Figure 8. RBS thickness calculations were performed using a model based approach which assumes bulk densities for both Ge and GeO\textsubscript{2}. The modeled thicknesses were then adjusted to account for the differences between the bulk densities and those calculated via XRR. Note that a rate measurement for Γ = 0.25 was not included since the bulk densities of the mixed-valent compounds within the film are unknown.
Figure 6. Density values for varying levels of $\Gamma$, measured via XRR analysis. Dotted lines indicate bulk densities for Ge (top) and GeO$_2$ (bottom).
Figure 7. Measured XRR spectra (black) and calculated spectra (red) for $\Gamma=1.00$ (a) and $\Gamma=0.00$ (b). Calculations were performed using the Rigaku GlobalFit software package.
Figure 8. The dependence of deposition rate of GeO$_x$ films with the oxygen gas fraction, $\Gamma$. Data are plotted from results using spectroscopic ellipsometry (SE), green squares; x-ray reflectivity (XRR), blue circles; and Rutherford backscattering spectrometry (RBS), red triangles.

As shown in Figure 8, the deposition rate from both ellipsometry and XRR data is 23 nm/min when $\Gamma=0.00$. The value obtained from RBS was somewhat lower, most likely due to a lower film density than the bulk value used in the calculation (Table 3). Upon increasing $\Gamma$ to 0.25, the deposition rate rose to 47 nm/min. This increased rate is directly related to the larger ion-induced secondary electron emission coefficient of oxide compounds on the surface of the germanium sputter target [36]. The deposition rate remained relatively constant for $\Gamma=0.50$, but dropped precipitously to a value of 7 nm/min for $\Gamma=0.75$ (15 sccm O$_2$, 5 sccm Ar), and remained low (5 nm/min) for $\Gamma=1.00$. This reduction in deposition rate is the result of the formation of higher order germanium-oxide compounds on the surface of the target. At a working pressure of 0.67 Pa (5 mTorr)
and a $\Gamma$ of 0.75 and above, the plasma flux can no longer react with the amount of oxygen present within the chamber, leading to oxygen adsorption onto the target surface. The reduction of the deposition rate associated with the formation of germanium-oxide is believed to be a direct result of the decreased sputter yield associated with the covalently bonded compound. The agreement between the deposition rates using the different techniques is remarkably good. The measured film thicknesses and deposition rates using SE, XRR and RBS are listed in Table 2 and Table 3, respectively. Note that the behavior of the deposition rate of GeO$_x$ as a function of oxygen partial pressure is similar to those measured in studies conducted by Lange et al. and Vega et al. [7,8]. However, the maximum deposition rates for stoichiometric GeO$_2$, calculated by Lange et al. and Vega et al., indicate growth rates of 180 nm/min [7] and 15 nm/min [8], respectively, and these largely disparate values are likely the result of their differences in chamber configuration, cathode size, applied power, and working distance.

Table 2. GeO$_2$ film thickness, $d$, as a function of oxygen gas fraction measured using SE, XRR and RBS.

<table>
<thead>
<tr>
<th>Oxygen gas fraction, $\Gamma$</th>
<th>$d_{SE}$ (nm)</th>
<th>$d_{XRR}$ (nm)</th>
<th>$d_{RBS}$ (nm)$^a$</th>
<th>$d_{RBS}$ (nm)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>112</td>
<td>108</td>
<td>63</td>
<td>72</td>
</tr>
<tr>
<td>0.25</td>
<td>112</td>
<td>111</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.50</td>
<td>110</td>
<td>106</td>
<td>102</td>
<td>126</td>
</tr>
<tr>
<td>0.75</td>
<td>101</td>
<td>109</td>
<td>90</td>
<td>112</td>
</tr>
<tr>
<td>1.00</td>
<td>101</td>
<td>107</td>
<td>92</td>
<td>115</td>
</tr>
</tbody>
</table>

$^a$Thickness calculated using bulk densities, 4.25 and 5.23 g/cm$^3$ for GeO$_2$ and Ge, respectively.

$^b$Thickness calculated using densities measured via XRR.
Table 3. GeO$_2$ film deposition rates, $r$, as a function of oxygen gas fraction measured using SE, XRR and RBS.

<table>
<thead>
<tr>
<th>Oxygen gas fraction, $\Gamma$</th>
<th>$r_{\text{SE}}$ (nm/min)</th>
<th>$r_{\text{XRR}}$ (nm/min)</th>
<th>$r_{\text{RBS}}$ (nm/min)$^a$</th>
<th>$r_{\text{RBS}}$ (nm/min)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>23.4</td>
<td>22.5</td>
<td>13.2</td>
<td>15.1</td>
</tr>
<tr>
<td>0.25</td>
<td>46.9</td>
<td>46.7</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.50</td>
<td>47.5</td>
<td>46.0</td>
<td>44.0</td>
<td>54.7</td>
</tr>
<tr>
<td>0.75</td>
<td>6.6</td>
<td>7.1</td>
<td>5.9</td>
<td>7.3</td>
</tr>
<tr>
<td>1.00</td>
<td>4.4</td>
<td>4.7</td>
<td>4.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

$^a$Thickness calculated using bulk densities, 4.25 and 5.23 g/cm$^3$ for GeO$_2$ and Ge, respectively.

$^b$Thickness calculated using densities measured via XRR.

3.4.2 Crystal structure and morphology

The x-ray diffraction patterns from the GeO$_x$ films grown as a function of $\Gamma$ did not show any features attributable to the films, showing that the GeO$_x$ films are all amorphous. The amorphous nature of the films is expected since the substrate temperature during growth is 100 °C. When the substrate temperature is this low, the period of the atomic jump process of adatoms on the substrate surface is very large, and the adsorbed species are unable to diffuse into energetically favorable positions characteristic of a crystalline lattice.

3.4.3 Chemical composition and Ge-valence state

The chemical valence state and surface chemistry of the grown GeO$_x$ films was analyzed by XPS. XPS survey spectra from three samples are shown in Figure 9. The survey spectrum from a film grown with $\Gamma$=1.00 shows contamination from carbon after exposure to the environment (Figure 9a) as well as the expected oxygen and germanium transitions. The effect of sputtering on the Ge chemistry was studied by comparing high energy resolution 3d and 3p spectra from the sputtered samples with the sputtered Ge
reference sample. The 3d spectra from a sputtered film grown with $\Gamma=1.00$ and the sputtered Ge reference sample are compared in Figure 10, where the chemical shift between Ge and GeO$_2$ can be seen, and also the fact that the GeO$_2$ is not reduced on sputtering with 2 keV Ne$^+$ ions. This lack of any preferential sputtering means that the composition can also be determined by quantifying the XPS spectrum of the sputtered GeO$_2$ film, where it was found that the Ge:O atomic ratio was 0.50 confirming that the film was indeed stoichiometric GeO$_2$.

Figure 9. XPS survey scans of (a) as-received GeO$_2$ grown at $\Gamma=1.00$, (b) the same film after sputtering with Ne$^+$ at 2 keV to remove surface contaminants, and (c) a Ge reference sample after sputtering with Ne$^+$ at 2 keV to remove surface contaminants. These spectra were taken in the PHI 5700 XPS using an analyzer pass energy of 187.85 eV.
Figure 10. Ge 3d XPS spectra from a Ge reference sample (solid line) and a film grown at \( \Gamma = 1.00 \) (dashed line), after sputtering with \( \text{Ar}^+ \) at 2 keV to remove surface contaminants. These spectra were taken in the SSI M-Probe using an analyzer pass energy of 100 eV.

High resolution XPS spectra were also taken at three different places on all films without any sputtering using the Kratos XPS. The energy scale was calibrated using Au and Cu, according to the procedures outlined by the ISO Standard, ISO 15472. Since C was present on the surface of these samples, all of these spectra could be calibrated with respect to the C 1s peak of adventitious carbon at a reference energy of 284.6 eV. Detailed analysis of the Ge 3d spectra from the sample grown at \( \Gamma = 0.25 \), showed the presence of GeO\(_2\), GeO and elemental Ge at the surface, Figure 11. Measured binding energies attributed to Ge (Ge\(^0\)), GeO (Ge\(^{2+}\)), and GeO\(_2\) (Ge\(^{4+}\)) were 29.0, 30.9, and 32.7 eV, respectively, and agree well with those reported by others using synchrotron radiation [102-104] and traditional XPS [102,104-106]. Some authors [102,105,107] have claimed that Ge\(^{1+}\) and Ge\(^{3+}\) states also exist in oxide films but peaks from these possible states were not needed and have not been included in the peak fits in this work.
Table 4. Composition measurement from spectra taken in the Kratos Ultra XPS using a monochromatic Al source. High energy resolution spectra were taken at a pass energy of 40 eV, and survey scans were taken with a pass energy of 160 eV. Spectra were acquired at 3 different places on each sample, averages are also shown. Note that all samples have been exposed to atmosphere prior to analysis, films shown in this table have not been sputtered.

<table>
<thead>
<tr>
<th>Oxygen gas fraction, Γ</th>
<th>High Energy Resolution Spectra</th>
<th>Survey Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>atomic %</td>
<td>atomic %</td>
</tr>
<tr>
<td></td>
<td>C1s</td>
<td>O1s</td>
</tr>
<tr>
<td>1.00</td>
<td>5.8</td>
<td>63.7</td>
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</tr>
<tr>
<td>average</td>
<td>5.8</td>
<td>63.3</td>
</tr>
<tr>
<td>0.75</td>
<td>5.7</td>
<td>64.9</td>
</tr>
<tr>
<td></td>
<td>5.8</td>
<td>64.4</td>
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<td></td>
<td>6.2</td>
<td>64.2</td>
</tr>
<tr>
<td>average</td>
<td>5.9</td>
<td>64.5</td>
</tr>
<tr>
<td>0.50</td>
<td>5.9</td>
<td>64.7</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>64.2</td>
</tr>
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<td>6.0</td>
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</tr>
<tr>
<td>0.25</td>
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<td></td>
<td>7.9</td>
<td>54.2</td>
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<td></td>
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<td>36.6</td>
</tr>
<tr>
<td>average</td>
<td>10.0</td>
<td>37.2</td>
</tr>
</tbody>
</table>
Figure 11. High energy resolution Ge 3d XPS spectra of GeO\textsubscript{x} films grown at (a) $\Gamma$=0.00, b) $\Gamma$=0.25, and (c) $\Gamma$=0.50. These spectra were acquired in the Kratos Ultra using an analyzer pass energy of 40 eV.

Further XPS analysis shows that films deposited for $\Gamma = 0.00$ were predominantly elemental germanium (29.0 eV) with a small amount of GeO\textsubscript{2} (32.7 eV) present as a surface oxide layer (Figure 11a), due to environmental exposure before XPS analysis. As mentioned above, at $\Gamma$=0.25, films were comprised of elemental Ge, GeO and a GeO\textsubscript{2} surface oxide layer (Figure 11b). Films deposited at higher O\textsubscript{2} gas fractions ($\Gamma \geq 0.50$) showed the presence of fully stoichiometric GeO\textsubscript{2}, without any reduced germanium-oxide species (Figure 11c). Note the obvious presence of the O 2s peak in Figure 11b and c.

High energy resolution XPS was also utilized to calculated the thickness of the native oxide on germanium films grown at $\Gamma$=0.00 by measuring the relative intensities of Ge 2p peaks corresponding to Ge$^{4+}$ and Ge$^{0}$ (Figure 12). For increased kinetic energy and escape depth, an Ag-L\textalpha source was used for comparison with results obtained using both Mg-K\textalpha and Al-K\textalpha sources. The results of the native oxide thickness calculations are shown in Table 5.
Figure 12. High energy resolution spectra of Ge 2p$_{1/2}$ (left) and 2p$_{3/2}$ (right) transitions for the film grown at $\Gamma=0.00$. Spectra were obtained using monochromated Ag-La (top) and Al-K\textalpha x-rays (bottom).

Table 5. Thickness, $d$, calculations for surface oxide layer of film grown at $\Gamma=0.00$, from intensities of Ge$^0$ and Ge$^{4+}$ components of Ge 2p$_{3/2}$ and 3d peaks using Mg, Al and Ag x-ray sources. Thicknesses were calculated from the method reported by Seah et al.$^c$
Inelastic mean free paths were calculated from NIST Standard Reference Database 71.

<table>
<thead>
<tr>
<th>x-ray Source</th>
<th>Transition</th>
<th>Electron Kinetic Energy(eV)</th>
<th>Inelastic Mean Free Path (nm)</th>
<th>$I_F$ (GeO$_2$)$^a$ (CPS eV)</th>
<th>$I_S$ (Ge)$^b$ (CPS eV)</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Ge 2p$_{3/2}$</td>
<td>266</td>
<td>0.79</td>
<td>307460</td>
<td>217804</td>
<td>0.7</td>
</tr>
<tr>
<td>Mg</td>
<td>Ge 3d</td>
<td>1221</td>
<td>2.31</td>
<td>8203</td>
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<td>0.7</td>
</tr>
<tr>
<td>Al</td>
<td>Ge 3d</td>
<td>1454</td>
<td>2.64</td>
<td>16339</td>
<td>58584</td>
<td>0.7</td>
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<tr>
<td>Ag</td>
<td>Ge 2p$_{3/2}$</td>
<td>1763</td>
<td>3.07</td>
<td>470</td>
<td>1427</td>
<td>0.9</td>
</tr>
</tbody>
</table>

$^a$Intensity attributed to oxide film layer, GeO$_2$

$^b$Intensity attributed to substrate layer, Ge

The RBS spectra of three GeO$_x$ films are shown in Figure 13. The backscattered ions observed are due to scattering by Ge (and O) in the film and Si from the substrate. The scattering from Ge, the heaviest among the elements present, occurs at the highest backscattered energies as shown in the RBS spectra (Figure 13). The measured height and width of this peak is related to the concentration and thickness distribution of Ge atoms in the (oxide) film and serves as a check since known Rutherford scattering cross section and experimental parameters can be used to calculate the composition and areal density of the films [100,101]. The experimental spectra along with the simulated spectra calculated using SIMNRA code are shown in Figure 13, and it can be seen that the simulated spectra calculated using the experimental parameters are in good agreement with the measured RBS spectra. The film thicknesses can be calculated from the aerial densities if the bulk densities are known. Here the Ge and GeO$_2$ bulk densities were used to calculate the initial thickness, and were then modified to reflect the film densities measured via XRR (Figure 8.), except for $\Gamma$=0.25 where the density of the mixed-valent composition is not known.
Figure 13. RBS spectra of GeO\textsubscript{x} films grown at (a) $\Gamma$=0.00, (b) $\Gamma$=0.25, and (c) $\Gamma$=1.00. The experimental and simulated spectra are shown for each value of $\Gamma$. The energy scale is 2 keV times the channel number.
Figure 13 shows that films grown at $\Gamma=0.00$ produce only a Ge peak (and Si from the substrate). No signal due to oxygen is detected, indicating that the film consists entirely of Ge on the Si (100) substrate. For films grown with oxygen, theoretical stoichiometries of germanium compounds, namely GeO [Ge$^{2+}$] and GeO$_2$ [Ge$^{4+}$], were considered. Stoichiometries of GeO and GeO$_2$ correspond to an O/Ge atomic ratio of 1 and 2, respectively. The O/Ge atomic ratios calculated from the RBS spectra are 1.04, 2.10, 2.16 and 2.20 for $\Gamma=0.25$, 0.50, 0.75 and 1.00, respectively. This shows that the film grown at $\Gamma=0.25$ has a significant contribution of GeO (or other reduced species). The values for $\Gamma=0.50$, 0.75 and 1.00 are somewhat higher than the expected stoichiometry of the films, a potential result of a slight fit error induced by noise present in the oxygen peak.

Thus the RBS and XPS analyses together confirm that the films formed at $\Gamma=0.00$ are Ge, the transition to mixed oxide composition (Ge+GeO+GeO$_2$) occurs at $\Gamma=0.25$ (Figure 11b and Figure 13b), and further increase in $\Gamma$ to 0.50 and above results in the formation of stoichiometric GeO$_2$ films.

3.5 Optical constants

Optical constants were measured and calculated using a general oscillator model consisting of two Tauc-Lorentz oscillators [108] as well as the Cauchy dispersion equation [109], represented by Equations 11-13.

$$
\epsilon_2(E) = 2nk = \frac{AE_0 C(E - E_g)^2}{(E^2 - E_0^2)^2 + C^2 E^2} \cdot \frac{1}{E}
$$

(11)
\[
    n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}
\]

(12)

\[
    k(\lambda) = \alpha \exp \left( \beta \left[ 12400 \left( \frac{1}{\lambda} - \frac{1}{\gamma} \right) \right] \right)
\]

(13)

The latter model (Cauchy dispersion) was used for optically transparent GeO\(_2\) on account of its negligible extinction coefficient and its decaying refractive index associated with increasing wavelength [109]. The former model (Tauc-Lorentz) was able to account for the free carrier absorption associated with amorphous germanium, allowing for the determination of optical constants for films with minimal oxygen concentration [37]. Note that the GeO\(_x\) layer was considered to be uniform for all models.

The optical constants, namely index of refraction (n) and extinction coefficient (k), and their dispersion behavior are shown in Figure 14a and b, respectively. As expected, films deposited using 0.0 sccm of O\(_2\) (\(\Gamma=0.00\)) have very high n throughout the measured spectral region (Figure 14a), reaching a maximum of 5.09 at 810 nm. Additionally, this film is shown to be highly absorbing (k>0) (Figure 14b), with the extinction coefficient decreasing as it approaches the theoretical band edge of 0.67 eV (1850 nm). At a flow rate of 5 sccm O\(_2\) (\(\Gamma=0.25\)), it can be noted that both n and k are lower than for \(\Gamma=0.00\). The behavior of the optical dispersion indicates that it consists of a mixture of elemental germanium as well as GeO\(_2\) and/or GeO. The optical behavior of the film is consistent with the transition regime between an elemental germanium target and a target coated with an oxide. The optical properties of the as-deposited GeO\(_x\) films at \(\Gamma=0.25\) are indicative of phase separation between oxygen rich GeO\(_x\) and Ge [110]. These findings are further corroborated by the results of the core-level binding energy
analysis (XPS), where the films were found to have a mixed composition of Ge+GeO+GeO₂.

Figure 14. The dispersion profiles for (a) refractive index, and (b) extinction coefficient, for GeOₓ films grown at the different values of Γ. Films deposited at oxygen flow rates of 20.0, 15.0 and 10.0 sccm of O₂ (Γ=1.00, 0.75, 0.50) displayed optical properties that were almost indistinguishable from one another. These films, all modeled using the Cauchy dispersion layer, displayed a
negligible extinction coefficient throughout the measured wavelength region as well as a refractive index that was shown to decrease as a function of increasing wavelength. These films display minimal dispersion, with their respective refractive indices varying from 1.66 to 1.60 within the wavelength region from 380 to 1700 nm. The measured refractive index values for these films are consistent with index values of 1.63 to 1.58, as reported by Vega et al. for wavelengths ranging from 270 to 870 nm [8].

3.6 Structure-optical property correlation

The effect of oxygen fraction during reactive deposition on the chemistry and optical properties of GeO$_x$ films can be understood and the processing parameter-chemistry-property relationship can be derived from these results. The semiconducting, amorphous Ge films, grown at $\Gamma$=0.00, exhibit a high refractive index (n) and a high extinction coefficient that decays as the wavelength approaches the theoretical band-edge at 1850 nm. As oxygen is introduced into the reactive gas mixture, Ge-O phases begin to form. Subsequently, oxide phases in the films induce changes in the oxidation state of Ge, which are responsible for the observed decrease in the refractive index and extinction coefficient of the films. A minimum $\Gamma$ of 0.50 is required to facilitate the formation of fully oxidized (GeO$_2$) films. Oxygen content less than this value will result in the formation of absorbing, sub-stoichiometric GeO$_x$, as corroborated by XPS and RBS analyses. Such samples exhibit refractive indices between those reported for pure Ge and GeO$_2$ films. Furthermore, the Ge-to-GeO$_2$ semiconductor-to-insulator transition, shown to occur with increasing oxygen content, serves to further reduce the films’ refractive indices. The proposed mechanism and correlation between the processing parameters, chemistry and optical behavior is presented in Figure 15. The aforementioned diagram
indicates the three different zones where pure Ge, mixed oxides, and GeO\textsubscript{2} films can be obtained by controlling the oxygen fraction during deposition. This proposed structure-property correlation is expected to be quite useful for tuning the process parameters to selectively control stoichiometry and subsequent optical behavior of magnetron sputtered Ge-O compounds.

![Graph showing the dependence of refractive index (n) on oxygen gas fraction (\(\Gamma\)) at a wavelength of 632 nm. The approximate regions for different film compositions are shown by the dashed lines.](image)

Figure 15. The dependence of refractive index (n) on oxygen gas fraction (\(\Gamma\)) at a wavelength of 632 nm. The approximate regions for different film compositions are shown by the dashed lines.

3.7 Conclusions

Germanium oxide (GeO\textsubscript{x}) films were grown by direct-current (DC) magnetron sputter-deposition over a wide range of oxygen flow rates. The effect of oxygen gas fraction in the reactive gas mixture significantly affects the chemical composition and optical properties of GeO\textsubscript{x} films. Structural analysis using x-ray diffraction confirms that
all of the GeO$_x$ films were amorphous. The chemical state of Ge and the overall stoichiometry of the films exhibit an evolution from pure Ge to a Ge+GeO+GeO$_2$ mixed phase and then finally to GeO$_2$ with increasing oxygen fraction from 0.00 to 1.00. Γ values of 0.50-1.00 were necessary to obtain stoichiometric GeO$_2$ films. Additionally, the effect of Γ is significant on the optical constants of GeO$_x$ films. The transition from pure, semiconducting germanium to mixed phase Ge+GeO+GeO$_2$ composition was associated with a characteristic decrease in refractive index (λ=550 nm) from 4.67 to 2.62 at Γ=0.25. Finally the refractive index drops to 1.60 for Γ=0.50-1.00, for fully stoichiometric GeO$_2$ films, corresponding to a valence state of 4+. A correlation between the O$_2$ gas fraction (Γ), chemical composition (Ge chemical state) and optical properties (n and k) of DC sputtered GeO$_x$ films has been established (Figure 15). Such a correlation should be useful to select the processing conditions in order to tune the chemical composition, and hence, the optical constants of GeO$_x$ films.
4. DEPOSITION AND CHARACTERIZATION OF MODULATED PULSE POWER MAGNETRON SPUTTERED MOLYBDENUM OXIDE (MoO<sub>x</sub>) FILMS

4.1 Introduction

Molybdenum oxide thin films find use in many technological areas including catalysis [40-44], optics [111,112], electronics [36,44,47-53], and chemical sensing [36,44,57-59], to name a few. The diversity of these applications can be attributed to the wide range of oxidation states (0-6+) accommodated by molybdenum [41,44,113] and the facile manipulation of those states via oxidation or reduction. In its fully oxidized state (6+), molybdenum trioxide (MoO<sub>3</sub>) is optically transparent with an optical band gap that ranges from 2.67-3.12 eV [36,44,114]. MoO<sub>3</sub> also exhibits dynamic coloration via reduction induced by UV irradiation (photochromism) [36,44], charge injection (electrochromism) [36,37], or heat treatment (thermocoloration) [115]. Additional oxide compounds formed by molybdenum include the “surface phase” Mo<sub>2</sub>O<sub>5</sub> (Mo<sup>5+</sup>), which has no known bulk structure [116-118], and MoO<sub>2</sub> (Mo<sup>4+</sup>), commonly present in the distorted rutile structure [119]. While not as widely investigated as MoO<sub>3</sub>, MoO<sub>2</sub> is electrically conductive and has shown significant promise for use as an anode material within lithium ion batteries [120-124].

As a result of the breadth of their technological applications, several physical vapor deposition methods for fabricating molybdenum oxide thin films have been explored. Such methods include, but are not limited to, spray pyrolysis [125-127],
thermal evaporation [37,128,129], pulsed laser deposition [130-132], radio frequency magnetron sputtering [133,134], and reactive DC magnetron sputtering [36,60,114,130,135]. While all of the aforementioned techniques are capable of depositing high quality films when performed under optimal conditions, studies employing reactive DC magnetron sputtering have generated significant interest due to the industrial scalability of magnetron sputtering techniques, as well as the high degree of control over the oxidation state as a function of reactive oxygen availability [36,60,114,130,135]. Previous works of note include studies performed by Mohamed et al. demonstrating a comprehensive correlation between oxygen partial pressure and the resulting crystallinity, chemistry, and optical behavior of molybdenum oxide thin films [36]. While numerous studies have confirmed that it is possible to obtain high quality molybdenum oxide thin films via DC magnetron sputtering, the advent of a technique known as modulated pulse power magnetron sputtering (MPPMS) has shown promise for further optimization. Specifically, the high target power densities, (~500 W/cm²) associated with MPPMS are capable of achieving a highly metallic deposition flux [4,19,20]. Reports by Hala et al. have indicated that the high power densities and variable pulse profiles associated with the MPPMS process are directly correlated to reduction in process instability associated with the formation of a dielectric, or “poisoned” surface oxide layer on the sputter target [4]. In addition, ion bombardment associated with MPPMS has been reported to improve film adhesion, while reducing surface roughness and providing increases in density [4,19,136]. Finally, a high degree of control over the magnitude and duration of MPPMS discharge events has been reported to reduce arcing, limit hysteresis when sputtering in reactive regimes, and tailor ionization levels of both
inert, reactive, and metallic components in the plasma [4,19,21-25]. The ability to leverage ionization levels of both reactive and metallic components could be of considerable benefit for controlling the chemistry and structure of molybdenum oxide thin films.

This study was performed to analyze the effect of systematic changes in the oxygen flow rate on the structural, chemical, and optical properties of thin (< 60 nm) molybdenum oxide films deposited using MPPMS. Of particular interest is the potential application of molybdenum oxide in optical interference coatings where smooth, amorphous, thin, transparent, variable index materials are desirable. To our knowledge, there are currently no reports on the deposition and characterization of MPPMS deposited oxides of molybdenum.

4.2 Materials and methods

4.2.1 Experimental conditions

Molybdenum oxide films were deposited within a stainless steel high-vacuum chamber equipped with multiple magnetron sputtering sources. Prior to deposition, the chamber was evacuated to a base pressure of at least 4.0x10^-5 Pa (3.0x10^-7 Torr). All magnetron guns were retracted and films were deposited using a single, 50 mm source placed 9 cm from the surface of the substrate. A working pressure of 1.33 Pa (10 mTorr) was maintained throughout all depositions. Due to the variations in pressure associated with the use of reactive gasses [3,7,137,138], pumping speed was varied between 25 and 28 L/s using an automated conductance controller. The source material was a 99.99% pure molybdenum target (K.J. Lesker) magnetically attached to a 50 mm diameter, unbalanced magnetron source (MeiVac, Inc.). Films were deposited on prime grade 50
mm dia. (001), p-type silicon wafers (University Wafer LLC) and also on 25 mm diameter quartz discs (Machine Glass Specialists Inc.) for the optical transmission measurements, with no bias or external heating applied to the substrates. The substrates were rotated at 8 rpm to reduce anisotropy imparted by the sputtering process.

Research grade argon (Airgas, 99.999%) and oxygen (Wieler Welding Co., 99.999%) facilitated the reactive sputtering process. The oxygen flow rate \((Q_{O2})\) and argon flow rate \((Q_{Ar})\) were controlled using two MKS mass flow controllers with a maximum flow rate of 20.00 +/- 0.04 sccm. The MPPMS process used a Zpulser AXIA™ magnetron discharge generator operated in manual mode with the capacitors charged to 300 V and a macropulse frequency of 50 Hz. MPPMS is a derivative of the high power impulse magnetron sputtering (HIPIMS) technique introduced by Kouznetsov, et al. in 1999 [139]. Both techniques utilize high target power densities at duty cycles less than 10% [22,23,139,140]. Key differences between the two techniques involve the shape, duration and magnitudes of the voltage pulses applied to the cathode. HIPIMS, consisting of square voltage pulses lasting less than 200 μs, achieves target power densities on the order of 1-3 kW/cm² [4,20,136,140]. MPPMS, on the other hand, is slightly less aggressive, utilizing longer overall pulses (>1 ms) at power densities approaching 500 W/cm² [4,19,20]. Unlike HIPIMS, the voltage pulses applied in the MPPMS technique consist of multiple microsecond-length pulses, known as “micropulses”, rather than just one square pulse. Micropulses typically last between 1 and 15 μs and can be varied with high precision to allow for the user to specify their frequency. The frequency of the microscale pulse application is directly related to the magnitude of the longer (>1 ms) macroscale voltage pulse [21,22,136]. A two part pulse
was created similar to that specified by Hála et al. [4]. The first stage of the pulse generated a low energy plasma discharge with a duration of 400 μs derived from a 20% micropulse duty cycle, and the second stage consists of a higher energy plasma lasting 600 μs controlled by micropulses applied at a 54.5% duty cycle with an on time of 12 μs and an off time of 10 μs as illustrated in Figure 16. The total macroscale duty cycle for the MPPMS deposition process was 5%. During depositions, the MPPMS power supply was operated in constant voltage mode and normalized to obtain an average power of 80 W at $Q_{O_2} = 0$ sccm. Changes in voltage and current output were analyzed using a Tektronix DPO 5204 multi-channel oscilloscope.

Time averaged optical emission spectroscopy (OES) allowed qualitative analysis of the relative concentrations of Ar and Mo species in the plasma discharge. Optical emission generated during the deposition process was collected by an external fiber optic placed directly before a quartz viewport 45 cm from the plume. Spectra were processed with an OceanOptics USB 4000 spectrometer using an integration time of 500 ms and dark correction to reduce the effects of ambient light prior to plasma ignition.
Figure 16. Pulse generation via MPPMS. The thin line represents voltage signal on and off time generated by the power supply, the bold line is the resulting cathode voltage.

4.2.2 Chemical, optical and structural characterization

Characterization of the structure of these films used multiple analysis methods. Surface roughness was quantified using a Veeco Instruments atomic force microscope (AFM) with a NanoScope V controller. Five regions were selected and scanned in tapping mode with a scan area of 25 µm². To determine the film thickness and optical dispersion, \textit{in situ} spectroscopic ellipsometry data were collected throughout the deposition process using a J.A. Woollam M2000VI ellipsometer that operated in the 380 – 1700 nm wavelength range. Surface roughness (AFM) and thickness (ellipsometry) measurements were verified with x-ray reflectivity (XRR) (Rigaku SmartLab).

Crystallinity was measured with grazing incidence x-ray diffraction (GIXRD) (Rigaku SmartLab) using an incidence angle of 0.35°, resolution of 0.01°, and a detector angle of 2θ. The x-ray source, Cu Kα (1.5418 Å), was operated at 40 kV and 44 mA. Optical transmission and reflectivity data were measured with a Perkin-Elmer Lambda 1050
UV/Vis/NIR spectrophotometer with an integrating sphere attachment. Transmission and reflectivity values were used in the calculation of the optical gap, $E_g$.

Surface analysis via x-ray photoelectron spectroscopy (XPS) was employed in order to analyze the composition and chemistry of the films. All scans were collected using a Physical Electronics 5700 XPS with a monochromatic aluminum x-ray source at a photon energy of 1486.7 eV. Survey scans were taken at an analyzer pass energy of 187.85 eV, while high resolution scans used a pass energy of 29.35 eV. Survey scans were taken for binding energies from 0 to 1400 eV, while high energy resolution scans capturing the molybdenum 3d doublet, were acquired from 220 to 245 eV. For convenience, all spectra were energy calibrated with respect to the adventitious carbon 1s transition at a binding energy of 284.6 eV. Fitting of the XPS spectra employed the CasaXPS 2.3.16 software package [82]. Parameters including full width at half maximum peak height, location of peak center and peak area were determined after using a Shirley background subtraction. A mixed Gaussian-Lorentzian line shape was used for the peak fitting.

4.3 Results and discussion

4.3.1 Reactive magnetron sputtering of molybdenum oxide

As the oxygen flow rates varied, the changes in the voltage and current evolved from the plasma discharge were monitored. An average power of 80 W with $Q_{Ar} = 20$ sccm and $Q_{O2} = 0$ operating at 1.33 Pa (10 mTorr) yielded an average power of 1600 W per pulse. The average power per pulse is calculated by dividing the total average power of 80 W by the 5% duty cycle. The oxygen flow rates used for deposition were selected by measuring the onset of target poisoning, wherein the entire target surface is coated
with molybdenum-oxygen compounds. The transition from a metallic target surface to an oxidized target surface is accompanied by a precipitous drop in both current and deposition rate [3,137,141]. Power levels were plotted as a function of oxygen flow rate, which was increased from 0.00 to 2.00 sccm, at intervals of 0.25 sccm (Figure 17). The total flow rate ranged between 20 and 22 sccm depending on the amount of oxygen added to the chamber. In order to maintain a working pressure of 1.33 Pa (10 mTorr) under different flow rates, the pumping speed was adjusted from 25 to 28 L/s. A dwell period of 90 seconds was used at each flow rate prior to recording the voltage and current. Upon fully poisoning the target at $Q_{O_2}=2.00$ and $Q_{Ar}=20.00$ sccm, $Q_{O_2}$ was then reduced to zero at increments of 0.25 sccm. Reduction of $Q_{O_2}$ was performed in order to analyze the change in oxygen content required to remove the oxide layer from the target. As Figure 17 illustrates, a measurable degree of hysteresis exists between the flow rates required to poison the target and those necessary to recover the metallic target surface. At $Q_{O_2} \leq 0.75$ sccm, the plasma flux acts as a getter, reacting with all of the oxygen within the chamber; however, once $Q_{O_2}$ exceeds 0.75 sccm, the excess oxygen that is not reacting within the deposition flux begins to adsorb onto the chamber surfaces, including the surface of the target.
Figure 17. Power output as a function of increasing (solid circles) and decreasing (open circles) oxygen flow rates for MPPMS.

Compound formation on the target surface, in this case oxidation, leads to a reduction in the net power achieved by the plasma discharge. At values of $Q_{O_2} \geq 1.25$ sccm the power evolved is no longer affected by the changing oxygen flow, indicating that the target surface has fully reacted. As shown in Figure 17, it is evident that the initial drop in power occurs at $Q_{O_2} = 0.75$ sccm. Figure 17 demonstrates that the power output for the MPPMS technique drops precipitously at a $Q_{O_2} = 1.00$ sccm. The rapid loss of power, coinciding with decreased current, is a result of several factors. First, the introduction of oxygen within the chamber reduces the number of free electrons within the plasma as a result of the formation of oxygen ions [38]. Additional losses in current are likely brought on by the inhibition of ion-induced secondary electron emission (ISEE) associated with compound formation on the target surface [4, 22, 25, 138, 142-144]. While documentation of the $Ar^+$ induced emission of secondary electrons for oxidized molybdenum is limited, studies by Depla et al. on the ISEE of Nb, Ta, and Re, have
indicated significant reduction in secondary electron emission as a result of surface oxidation [138]. Reduction of the number of secondary electrons emitted leads to a net decrease in electron density near the surface of the cathode, resulting in the occurrence of fewer ionization events responsible for sputtering [2,3,83,137,138]. Thus, surface oxidation appears to be the main factor in the decrease in current, and subsequently, deposition rate. The ISEE is a function of the ion energy; therefore it will be dependent upon the voltage applied to the cathode [4,138,142]. Note that instantaneous cathode voltage levels for films deposited at $0 \leq Q_{O_2} \leq 2$ sccm ranged from 550 to 610 volts.

4.3.2 Optical emission spectroscopy

Additional analysis of the effect of oxygen flow on power output and plasma discharge was conducted using optical emission spectroscopy (OES). Figure 18 contains the optical emission spectra of Ar and Mo when $Q_{O_2}= 0.0$ sccm and $Q_{Ar}= 20$ sccm as well as the spectra at $Q_{O_2}= 2.0$ sccm and $Q_{Ar}= 20$ sccm. Under these conditions, the relative concentrations of both excited argon (Ar I, 650-875 nm) and molybdenum peaks (Mo I, 300-610 nm) of the plasmas differ significantly. As a result of the high power density experienced by the target during MPPMS, the plasma appears highly metallic in character, with a relatively small contribution from Ar related optical emission. Further, the high target power density associated with MPPMS has the potential to cause target atom ionization [21,136,145-147], as evinced by peaks shorter than 280 nm attributed to singly ionized molybdenum (Mo II) [35]. These same peaks are not readily detectable in the optical emission attributed to the poisoned Mo target at $Q_{O_2}= 2.0$ sccm. In the poisoned regime ($Q_{O_2} \geq 1.25$ sccm) the magnitude of the optical emission signal from Mo
is greatly reduced. As expected, target oxidation and subsequent current reduction drastically reduces molybdenum photoemission within the plasma.

Figure 18. Optical emission spectra obtained for MPPMS plasmas. Data was collected during MoO_x depositions using oxygen flow rates of 0.00 sccm (top) and 2.00 sccm (bottom) and 20 sccm Ar for both. The saturation in the upper spectrum is a result of the collection time (500 ms) used to accommodate optical emission intensity.

4.3.3 X-ray photoelectron spectroscopy

XPS analysis was used to determine the composition and chemistry of MPPMS deposited samples that were fabricated at Q_{O2}=0.00, 0.75, 1.00, 1.25, and 2.00 sccm. For each specimen, a survey spectrum (Figure 19) and high resolution spectrum (Figure 20) were obtained. Chemical analysis using x-ray photoelectron spectroscopy indicated that the oxidation state and associated stoichiometry of the as-grown films was highly sensitive to the oxygen flow rate. Survey scans of representative films (Q_{O2}=0.00 to 2.00
scm) were acquired in order to quantify the presence of various elements within the films. Peak shapes and binding energies (Mo 3d) of high resolution scans were used to determine stoichiometry. All films analyzed via XPS were exposed to atmosphere prior to measurement since the growth and analysis chambers were separate. As a consequence of environmental exposure, all of the films analyzed contain 23 - 30 at% of adventitious carbon on their respective surfaces. Note that spectra were calibrated with respect to the carbon 1s transition with a binding energy of 284.6 eV.

Figure 19. Survey spectrum of fully stoichiometric MoO$_3$ deposited at an oxygen flow rate of 2.00 sccm O$_2$ and 20.00 sccm Ar at 1.33 Pa (10 mTorr).
Figure 20. High resolution XPS spectra of the Mo 3d transitions for depositions at flow rates of 0.00, 0.75, 1.00, 1.25, and 2.00 sccm O$_2$. Spectra are offset for clarity and the Mo 3d$_{5/2}$ peaks are labeled.

High energy resolution XPS yielded detailed information regarding the oxidation state of the molybdenum. The presence of oxidation state Mo$^{6+}$ was indicative of the compound MoO$_3$, while the presence of Mo$^{5+}$ and Mo$^{4+}$ was associated with sub-stoichiometric compounds including Mo$_2$O$_5$ and MoO$_2$ (Table 6) [37,41,56,60,81,114,148-150]. Furthermore, at Q$_{O_2} < 1.00$ sccm, metallic Mo was also present. It is highly likely that small quantities of additional sub-oxides were present within the films; however, their presence was indistinguishable from the uncertainty
inherent in the peak fitting process. In the case of multiple doublets resulting from the
presence of different oxidation states, the doublet spacing (3.13 eV) [81] and peak area
ratios were kept constant during peak fitting. The area of the 3d_5/2 peak was constrained
to be 1.5 times that of the peak associated with the 3d_3/2 transition [81,109]. In order to
account for the asymmetry inherent in the 3d transition for metallic Mo, 3d transitions
from an experimentally obtained Mo reference were measured and subsequently used to
perform fits. Films deposited at Q_{O2}=0.00 and 0.75 sccm were found to be mostly
metallic in character, and the presence of the Mo^{5+} and Mo^{4+} oxidation states was the
result of environmental exposure, as subsequent analysis after one minute of ion beam
sputtering produced spectra consistent with that of metallic molybdenum. According to
data obtained from high resolution spectra, molybdenum trioxide films were only
obtainable at oxygen partial pressures at or above the threshold for target poisoning,
corresponding to Q_{O2}=1.25 sccm.

Table 6. Binding energies (eV) for various oxidation states of molybdenum.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Valence</th>
<th>Binding Energy (eV)</th>
<th>Reference Values (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO_3</td>
<td>6</td>
<td>235.72, 232.59</td>
<td>235.70, 232.51</td>
</tr>
<tr>
<td>MoO_2</td>
<td>5</td>
<td>234.69, 231.56</td>
<td>234.36, 231.17</td>
</tr>
<tr>
<td>MoO_2</td>
<td>5</td>
<td>232.64, 229.51</td>
<td>231.8, 228.7</td>
</tr>
<tr>
<td>Mo</td>
<td>0</td>
<td>231.38, 228.25</td>
<td>231.13, 228.00</td>
</tr>
</tbody>
</table>

4.3.4 Spectroscopic ellipsometry

Analysis of data collected from in situ spectroscopic ellipsometry (SE) provided
values for the thickness and the real (n) and imaginary (k) components of the refractive
index. To obtain these values, the raw amplitude (\(\psi\)) and phase difference (\(\Delta\)) data
collected by the ellipsometer was fit with a general oscillator model containing a Cauchy layer; a model commonly used for high energy optical gap materials such as molybdenum trioxide, due to the minimal absorption ($k \approx 0$) as well as exponential decay of the refractive index ($n$) as a function of decreasing photon energy [109]. The optical constants of films deposited in the poisoned regime ($Q_{O2} > 1.00$ sccm) were modeled using a general oscillator model with two Tauc-Lorentz oscillators to account for the free-carrier absorption associated with substoichiometric molybdenum oxide compounds, $\text{Mo}_2\text{O}_5$, $\text{MoO}_2$, and metallic $\text{Mo}$ and their respective oxidation states, $5^+$, $4^+$, and 0. Film thicknesses were also determined as well as the deposition rates, given in Table 7.

Table 7. Thickness ($d$) and deposition rate ($r$) for molybdenum oxide films deposited at varying oxygen flow rates ($Q_{O2}$) Note: $Q_{Ar}=20$ sccm.

<table>
<thead>
<tr>
<th>$Q_{O2}$ (sccm)</th>
<th>$d$ (nm)</th>
<th>$r$ (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>0.75</td>
<td>28</td>
<td>19</td>
</tr>
<tr>
<td>1.00</td>
<td>52</td>
<td>13</td>
</tr>
<tr>
<td>1.25</td>
<td>52</td>
<td>11</td>
</tr>
<tr>
<td>2.00</td>
<td>53</td>
<td>7</td>
</tr>
</tbody>
</table>

Metallic-rich films deposited at $Q_{O2} < 1.25$ exhibit characteristically higher $n$ and $k$ values than fully oxidized samples deposited in the poisoned regime ($Q_{O2} > 1.00$), similar to that described by T. He and J. Yao [44]. As shown in Figure 21a, in the visible to near IR spectral range (380 – 1700 nm) the $n$ of the metallic samples spans from a minimum of 2.1 at 381 nm to 3.7 at 760 nm. At wavelengths greater than 1200 nm, the index slightly fluctuates around a value of $n = 2.5$. The $\text{MoO}_3$ films prepared in the
poisoned target regime, have the same index as the metallic films at $\lambda = 380$ nm; however, the index gradually decreases to a constant value of 1.86 starting at 800 nm and remains nearly invariant through 1700 nm. Additionally, those films have negligible extinction coefficients ($k < 1 \times 10^{-3}$) at energies below the onset of the absorption edge located at 506 nm (Figure 21b). In contrast, the $k$ of films fabricated in the non-poisoned regime, increase from 3.1 to 7.5 with wavelength. Films deposited in the transition region between the metallic and poisoned regime ($Q_{O2} < 1.25$ sccm), exhibit optical dispersion that falls between that of the MoO$_3$ and metallic films.

![Figure 21. Refractive index, n, (a) and extinction coefficient, k, (b) for MoO$_x$ films deposited at oxygen flow rates of 0.00 sccm (solid line), 0.75 sccm (dashed line), 1 sccm (dotted line), 1.25 (dash-dot line) and 2.00 sccm (dash-dot-dot line).]
A plot of the refractive index and extinction coefficients as a function of $Q_{O2}$ at wavelengths of 632, 900 and 1200 nm (Figure 22) illustrates the effect of oxygen flow rate on the optical properties of the films. As the partial pressure of oxygen increases, the optical constants begin to change as a result of the transition between metallic and dielectric character. XPS measurements, as mentioned previously, show a clear effect on compound formation as a function of oxygen flow rate. Comparison of XPS data and optical measurements allows for the optical properties to be directly correlated to the compounds present within each film. At $Q_{O2}=0.00$ sccm and $Q_{Ar}=20.00$ sccm, the films are metallic in nature, with trace amounts of surface oxide compounds, $\text{MoO}_3$, $\text{Mo}_2\text{O}_5$, and $\text{MoO}_2$. An increase in oxygen flow to a rate of 1.00 sccm represents the onset of oxide formation on the sputtering target surface resulting in a noticeable decrease in both refractive index and extinction coefficient for the grown films. The drop in both refractive index and extinction coefficient is the direct result of the formation of $\text{MoO}_3$ ($\text{Mo}^{6+}$) as well as the reduced species $\text{Mo}_2\text{O}_5$ ($\text{Mo}^{5+}$). Formation of $\text{Mo}_2\text{O}_5$ can be associated with a marked increase in both $n$ and $k$, as shown in Figure 21 and Figure 22. Based on the data shown in Figure 20, it is evident that values of $Q_{O2}=1.25$ sccm or higher are necessary to form $\text{MoO}_3$ films without the presence of absorbing substoichiometric molybdenum-oxide compounds.
4.3.5 Transmission measurements and optical gap calculation

Spectral transmission and reflectance measurements were collected in order to quantify the optical gap of films deposited with the different oxygen flow rates. To determine the optical gap, the absorption coefficient, $\alpha$, was first determined using the measured spectral transmission and reflectivity. The optical gap ($E_g$) was calculated using the following equation [1, 27]:

$$a h \nu = B (h \nu - E_g)^{\eta}$$

(14)

where the exponent, $\eta$, varies based on the band-to-band transitions accommodated by a given material, $B$ is a constant (set equal to one in this case) and $h \nu$ is the photon energy. For molybdenum oxides, the exponent is 2, due to their intrinsic ability to facilitate
indirect-allowed band-to-band transitions [56,80,151]. A Tauc plot was then generated wherein \((αhν)^{1/2} \text{ (eV}^{1/2} \text{ cm}^{-1/2})\) was plotted as a function of photon energy, \(hν\) (eV). The optical gap \((E_g)\) was determined by extrapolating the linear portion of the plotted data to the corresponding photon energy where \((αhν)^{1/2}\) is equal to zero.

Table 8. Calculated optical gaps \((E_g)\) as a function of increasing oxygen flow rate \((Q_{O2})\)

<table>
<thead>
<tr>
<th>(Q_{O2} \text{ (sccm)})</th>
<th>(E_g \text{ (eV)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>2.12</td>
</tr>
<tr>
<td>1.25</td>
<td>2.45</td>
</tr>
<tr>
<td>2.00</td>
<td>2.74</td>
</tr>
</tbody>
</table>

The optical gaps listed in Table 8 indicate that \(E_g\) increases as a function of increasing oxygen flow. As shown in the high resolution XPS spectra (Figure 20) the oxidation state associated with both depositions at \(Q_{O2}=1.25\) and 2.00 sccm is 6+, indicative of fully stoichiometric MoO₃. Differences in \(E_g\) can potentially be attributed to the reduction of defects associated with the formation of the fully stoichiometric compound. Furthermore, the lower optical gap associated with the film deposited at \(Q_{O2}=1.00\) sccm was shown to contain substoichiometric Mo₂O₅ compounds associated with the presence of the 5+ valence state. The occurrence of the 5+ oxidation state was found via XPS analysis, as illustrated in Figure 20. Absorption attributed to the 5+ oxidation state is likely the result of charge transfer between the molybdenum and oxygen species [21, 78]. The presence of the further changes in the optical gap is a potential consequence of the formation of oxygen inclusions within the film, associated with higher \(Q_{O2}\) values. The optical gap of 2.74, obtained for the MoO₃ film deposited at
4.3.6 Structural characterization

Results of both atomic force microscopy (AFM) and x-ray reflectivity (XRR) analyses indicate the presence of sub-nanometer roughness for all films deposited. Although roughness values are low, there is a discernible difference in surface morphology for different oxygen flow rates. This is illustrated in Figure 23, where the root mean squared roughness, as determined by AFM increases with oxygen flow rate, ranges from 0.2 nm at $Q_{O_2}=0.00$ to a maximum value of 0.9 nm at $Q_{O_2}=1.00$ sccm. The increase in surface roughness with the onset of target poisoning is likely a direct result of repeated interruption of local epitaxy induced by the formation of a surface oxide layer, leading to continuous renucleation within the growing film [152,153]. AFM composite images shown in Figure 24 for three of the films provide visualization of this effect on surface morphology.
Figure 23. Surface roughness as a function of oxygen flow rate as determined by AFM. Lines are to guide the eye.

Figure 24. AFM composite images showing surface roughness and morphology of films deposited at oxygen flow rates of 0.00 (a), 1.00 (b), and 2.00 sccm (c). Images are of a 1 µm² area.
From XRR data the density of the films was determined from the total reflection or critical edge, film thickness was calculated from the period of the oscillations in the spectrum and surface roughness values were determined based on the rate of signal decay as a function of the detector angle (2θ). All calculations were performed using the Rigaku GlobalFit software package. Analysis of XRR data used a three-layer model consisting of silicon substrate, native silicon oxide layer, and the MoOₓ. Table 9 contains the surface roughness, density, and thickness data as determined by XRR. In addition to reflectivity measurements, grazing incidence x-ray diffraction (GIXRD) was performed on all samples. As illustrated in Figure 25, GIXRD analysis was able to show that the degree of crystallinity present within the films varied dramatically as a function of oxygen content. Films deposited at flow rates of 0.00 and 0.75 sccm O₂ demonstrated significant crystalline character, with peaks characteristic of body-centered cubic molybdenum located at \( \theta = 48.8^\circ \) (110), \( \theta = 58.9^\circ \) (200) and \( \theta = 74.1^\circ \) (211). At higher oxygen flow rates coinciding with the onset of formation of molybdenum oxides, the films are shown to be amorphous. Sharp crystalline peaks around \( \theta = 50.8^\circ \) present within those spectra are the result of x-ray interaction with the native oxide layer on the (100) silicon substrate [48].
Table 9. Surface roughness, density, and thickness of MoO₃ films, as determined by XRR.

<table>
<thead>
<tr>
<th>O₂ (sccm)</th>
<th>Density (g/cm³)</th>
<th>% of Bulk Density α-MoO₃</th>
<th>Surface Roughness (nm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>9.7</td>
<td>--</td>
<td>0.7</td>
<td>24.0</td>
</tr>
<tr>
<td>0.75</td>
<td>9.8</td>
<td>--</td>
<td>0.8</td>
<td>28.0</td>
</tr>
<tr>
<td>1.00</td>
<td>4.2</td>
<td>89.0</td>
<td>0.6</td>
<td>51.6</td>
</tr>
<tr>
<td>1.25</td>
<td>3.8</td>
<td>80.6</td>
<td>0.8</td>
<td>51.8</td>
</tr>
<tr>
<td>2.00</td>
<td>3.8</td>
<td>80.6</td>
<td>0.9</td>
<td>53.3</td>
</tr>
</tbody>
</table>

Figure 25. Grazing incidence x-ray diffraction (GIXRD) spectra of MoO₃ films deposited at varying oxygen flow rates as given in the figure. Peak assignments: body-centered cubic molybdenum: 2θ = 48.8° (110), 2θ = 58.9° (200) and 2θ = 74.1° (211); silicon dioxide: 2θ = 50.8° (003).
4.4 Conclusions

Deposition using MPPMS within the poisoned regime \( (Q_{O_2} \geq 1.25 \text{ sccm}) \) allowed for the fabrication of amorphous, transparent MoO\(_3\) with optical gaps of 2.45 and 2.74 eV at flow rates of 1.25 and 2.00 sccm O\(_2\), respectively. Spectroscopic ellipsometry studies of these films indicated negligible values for the extinction coefficient \((k)\) at energies below 2.45 eV. Fully stoichiometric MoO\(_3\) films, as verified by XPS analysis, were only obtained from sputter depositions where the target surface was fully poisoned. Films deposited at flow rates of 0.00 and 0.75 sccm O\(_2\) were shown to have higher densities, corresponding to elemental molybdenum \((10.18 \text{ g/cm}^3)[36]\) and crystalline structure associated with body center cubic Mo. Correspondingly, these films were the only specimens that possessed 3d transitions associated with Mo\(^0\) \((3d_{5/2} = 226.9 \text{ eV})\). Films deposited within the transition region, at 1.00 sccm O\(_2\), consisted largely of mixed Mo\(^{6+}\) and Mo\(^{5+}\) oxidation states, corresponding to MoO\(_3\) and Mo\(_2\)O\(_5\) compounds. The presence of the Mo\(_2\)O\(_5\) compound is associated with increased absorption and a net reduction of the optical gap to 2.12 eV. AFM and XRR analysis concluded that the surface roughness values were below one nanometer for all films, with roughness values increasing alongside oxygen partial pressure until reaching a maximum value at 1.00 sccm O\(_2\).

Based on measurement of density, absorption, and chemical state, it can be concluded that films deposited at oxygen flow rates at and below \(Q_{O_2}=0.75 \text{ sccm}\) are metallic, while films deposited at and above \(Q_{O_2}=1.00 \text{ sccm}\) were shown to be insulating.
5. DEPOSITION AND CHARACTERIZATION OF DC SPUTTERED RHENIUM OXIDE (Re₃O₇) FILMS

5.1 Introduction

Rhenium, a hexagonally close packed refractory metal, has several oxides that possess a variety of interesting optical and electronic properties. The commonly occurring oxides of rhenium are ReO₂, ReO₃, and Re₂O₇ [27, 67, 154-158]. The lowest valence oxide, ReO₂, is monoclinic in structure, while ReO₃ consists of a network of ReO₆ octahedra having a cubic, “perovskite-type” structure [26, 27]. Finally, Re₂O₇ consists of ReO₆ octahedra and ReO₄ tetrahedra, and has been reported to be highly hydroscopic, decomposing into perrhenic acid (HReO₄) upon exposure to moisture [61, 63, 154, 156]. The most widely investigated of these compounds is ReO₃, due to its metallic-like conductivity and its low absorption within the visible spectrum, both of which are similar to silver [27, 28, 159, 160]. The high conductivity \( \sigma_{\text{ReO}_3} = 10^3 - 10^4 (\Omega \text{ cm})^{-1} \) [28, 61] and minimal optical absorption are a direct consequence of the electronic configuration of ReO₃, which contains a single free electron within the 5d electron shell [26-29]. As a result of their unique optical and electronic properties, thin films of ReO₃ have been used for several diverse applications, including catalysis [62-66], interfacial layers for high temperature superconductors [61], anode buffer layers for polymer solar cells [67], and electrical contacts for liquid crystal devices [26]. Additionally, ReO₃ has ultraviolet (UV) absorption features centered at 310, 177, 155, 124 nm (4.7, 8 and 10 eV),
as well as the onset of free-electron absorption at 540 nm (2.3 eV) [27,28,160].
Interestingly, there are no dominant absorption features between 310-540 nm (2.3-4.0 eV), giving rise to a small transmission window within the visible region. Therefore, thin films of ReO$_3$ could also have promise as a transparent-conductive material in applications requiring a narrow transmission band.

Deposition of mixed-valent rhenium oxide thin films has been performed using radio-frequency (RF) magnetron sputtering [61], electrodeposition [67,157,158,161,162], evaporation from rhenium filaments [154], and reactive direct current magnetron sputtering (DCMS) [27]. At this time, there have been very few studies on the optical and chemical properties of rhenium-oxygen compounds deposited using reactive DCMS [27], which is the subject of this work. Work by Ghanashyam Krishna *et al.* has described a method of depositing rhenium-oxygen compounds using reactive DCMS, wherein the bias voltage is varied and its effect on the spectral reflectivity is systematically analyzed [27]. Results obtained by Ghanashyam Krishna *et al.* indicate that it is possible to use reactive DCMS to deposit 50-180 nm thin films that demonstrate optical behavior analogous to bulk ReO$_3$, as reported by Weaver *et al.* [28] and Feinlieb *et al.* [28]. However, to our knowledge, there are currently no studies reporting on the relationship between the chemistry and spectral (380-1700 nm) optical properties of mixed-valent rhenium oxide thin films deposited via reactive DCMS.

In this study, a method of maximizing the ReO$_3$ content within the films using *in situ* spectroscopic ellipsometry (iSE) was devised. *In situ* monitoring of the optical behavior, throughout film growth, allows for the selection of oxygen (Q$_{O_2}$) and argon (Q$_{Ar}$) flow rates capable of increasing ReO$_3$ content within the films. Process
optimization was achieved through real-time identification of characteristic absorption features, namely the minimization of the extinction coefficient, k, at wavelengths between 450 and 750 nm (1.65-2.75 eV). After establishing the deposition conditions required for maximizing ReO$_3$ content, analyses of the composition, phase distribution, and density, were performed via x-ray photoelectron spectroscopy (XPS) and x-ray reflectivity (XRR) in order to derive a comprehensive understanding of process-property relationships. XPS, XRR, and SE measurements were made \textit{ex situ} after one and thirty days exposure to atmosphere at ambient temperatures of 20-25 °C and relative humidity between 20 and 25%. Based on the aforementioned reports of instability [61,63,154,156], it is important to analyze environmental robustness prior to using ReO$_3$ thin films for applications requiring consistent optical performance and structural stability.

5.2 Materials and methods

5.2.1 Deposition

Rhenium oxide thin films were deposited within a stainless steel high vacuum chamber evacuated to a pressure of 5.3x10$^{-5}$ Pa (4x10$^{-7}$ Torr). A 3 mm thick, 50 mm diameter rhenium sputter target (99.99%, K.J. Lesker), was magnetically attached to a 50 mm magnetron source (MeiVac, MAK) at an angle of 20° with respect to the substrate normal. The distance between the target and the p-type silicon (100) (University Wafer LLC) substrate was 9 cm. During deposition, research grade O$_2$ (99.995%) and Ar (99.999%) were introduced via separate mass flow controllers, mixed prior to entering the chamber, and maintained at a total pressure of 1.33 Pa (10 mTorr) at a pumping speed of 25 L/s [83]. Oxygen and argon content were regulated by controlling the flow rates $Q_{O_2}$ and $Q_{Ar}$, while the total flow rate $Q_{TOT}$ was kept constant at 20 sccm. The oxygen
fraction $Q_{O2}$, represented by $Q_{O2}/Q_{TOT}$, was varied from $Q_{O2} = 0.0$-0.8 by increments of 0.1, while the optical constants were monitored every ten seconds using in situ spectroscopic ellipsometry. In situ data were gathered during continuous deposition for a period of one minute at each increment of $\Gamma$. Values of $\Gamma$ resulting in film layers with minimal extinction coefficients throughout the visible region were selected and used in the deposition of multiple films for further ex situ analysis. The films selected for ex situ optical and chemical analysis were deposited for three minutes at a cathode voltage $V_c = 631$ V and current $I_c = 80$ mA, resulting in an applied power of 50 W. Depositions took place upon a substrate platen set to rotate at 12 RPM to mitigate the anisotropy imparted by the sputtering process. Note that no heating, outside of thermal contributions from the plasma, was applied to the substrate.

5.2.2 Characterization

The optical constants of the rhenium oxide films were measured using a J.A. Woollam M2000VI spectroscopic ellipsometer (SE) at an angle of incidence of 70º, near the Brewster’s angle for silicon. The extinction coefficient (k) and the refractive index (n) were obtained upon fitting the raw polarization data to the Kramer’s Kronig consistent model described within section 3.4. Thickness values obtained through spectroscopic ellipsometry were verified using a KLA-Tencor stylus profilometer.

XPS was performed using a Physical Electronics 5700 equipped with an Al-Kα x-ray source operating at 1486.6 eV. The energy scale was calibrated using Au and Cu, according to the procedures outlined by the ISO Standard, ISO 15472. Survey scans were acquired at an analyzer pass energy of 187.85 eV (0.80 eV energy step) while high energy resolution scans of the core level Re 4f, Re 4s, C 1s, and O 1s transitions were
acquired at a pass energy of 29.35 eV (0.125 eV energy step). High energy resolution spectra were calibrated with respect to the rhenium 4f\textsubscript{7/2} transition, corresponding to the Re\textsuperscript{6+} valence state, at a binding energy of 44.9 eV, as reported by Tysoe \textit{et al.} [1]. The reference was used for all films in order to allow for any small electrical charging. To mitigate the level of error present in peak fittings, the spacing between the 4f\textsubscript{5/2} and 4f\textsubscript{7/2} components was constrained to reflect a spin-orbit splitting of 2.5 eV [81]. Additionally, the components of the 4f doublets were fit using equal full-width at half-maximum values, as well as area ratios of 3:4 (4f\textsubscript{5/2}:4f\textsubscript{7/2}) [19]. Shirley background subtraction and 70% Gaussian 30% Lorentzian line shapes were used to fit all spectra using the CasaXPS 2.3.16 software package [82]. To obtain a metallic reference for use in quantifying binding energy shifts, samples were sputtered for 5 minutes using a differentially pumped ion gun at 4 keV with an argon pressure of 10x10\textsuperscript{-3} Pa and an emission current of 25 mA. The binding energy obtained for the metallic Re\textsuperscript{0} 4f\textsubscript{7/2} peak was 40.3 eV, in agreement with values reported in the Physical Electronics \textit{Handbook of X-Ray Photoelectron Spectroscopy} [22]. Note that no sputtering was utilized prior to analysis of survey and high resolution scans due to this facile reduction of higher order rhenium-oxygen compounds during sputtering [163,164].

Electron micrographs were taken using an FEI Sirion scanning electron microscope (SEM). Measurements of the films’ densities were performed via x-ray reflectivity analysis (XRR) using a Rigaku Smartlab x-ray diffractometer, while grazing incidence x-ray diffraction (GIXRD) was also performed, indicating that all films deposited were amorphous. The observation of the films’ amorphous character is in
agreement with results obtained by Hahn et al. for cathodically electrodeposited ReO$_3$ thin films [158].

5.3 Results and discussion

5.3.1 *In situ monitoring of optical constants*

*In situ* ellipsometry measurement of rhenium oxide as a function of increasing oxygen content was used in order to determine the $\Gamma$ required to minimize $k$ within the visible region. Values of $\Gamma$=0.5 and 0.6 were shown to produce minimal values of $k$, as shown in Figure 26. Since oxides of rhenium are not dielectric, like many transition metal oxides, the onset of arcing and process instability as a function of increasing $\Gamma$ was not an issue.

![Figure 26. Extinction coefficient values, $k$, as a function of oxygen flow rate ratio, $\Gamma$, at wavelengths of 450, 600, and 750 nm.](image)
As shown in Figure 26, values of $k$ at 450, 600 and 750 nm, are consistent with reported values for metallic rhenium at $\Gamma$=0.0 [165]. As $\Gamma$ is increased, $k$ values continue to decrease until reaching $\Gamma$=0.4, where a slight increase in $k$ occurs as the potential result of the onset of absorption features related to lower valent rhenium species [162]. As $\Gamma$ continues to rise, to 0.5 and 0.6, the target surface begins to become increasingly coated with adsorbed oxygen, corresponding to a deposition environment conducive to the growth of ReO$_3$, as evinced by the characteristic reduction in $k$ between 450 and 750 nm [27,28,160]. Further augmentation of $\Gamma$, to 0.7 and above, lead to larger values of $k$. The observed increases in $k$ at $\Gamma>$0.6 are likely due to the formation of Re$_2$O$_7$, however, further work would be necessary to quantify the optical behavior of Re$_2$O$_7$ within this region. For depositions taking place at $\Gamma \geq 0.2$, the $k$ minima occur near 450 nm, with the lowest values, 0.2 and 0.6, corresponding to $\Gamma$=0.6 and 0.5, respectively. Diffuse reflectance studies of bulk, single crystal ReO$_3$ performed by Weaver et al. [160] and Feinleib et al. [28] reported values of $k_{450\text{nm}}$=0.0 and 0.2, respectively. Despite differences in morphology and crystallinity, good agreement exists between the in situ optical constants obtained at $\Gamma$=0.6 and reported values [28,160]. Therefore, for minimum $k$, rhenium oxide thin films were subsequently deposited at $\Gamma$=0.5 and 0.6 and characterized extensively using SEM, XRR, XPS and SE, as discussed below.

5.3.2 Microstructural characterization

Secondary electron micrographs of rhenium oxide films deposited at $\Gamma$=0.5 and $\Gamma$=0.6 are shown in Figure 27 after 30 days air exposure. The microstructure of the film deposited at $\Gamma$=0.5 shows a dendritic structure dotted with dark features that appear to be in the form of droplets (Figure 27a, inset). Rhenium oxide deposited at $\Gamma$=0.6 (Figure
27b) is shown to contain a large, interconnected network of cracks. These cracks appear to be a consequence of buckling induced by compressive stress as a result of the volumetric expansion of the film (Figure 27b, inset). Expansion and droplet formation are thought to be the result of the instability of Re$_2$O$_7$ ($\rho=6.10$ g/cm$^3$), forming HReO$_4$ ($\rho=2.15$ g/cm$^3$) upon exposure to moisture [18,156]. The films’ non-uniform microstructure and poor adhesion are similar to reports of instability associated with the presence of Re$_2$O$_7$ and perrhenic acid, HReO$_4$ [18,26,61,154,156,158].

Figure 27. Scanning electron micrographs for rhenium oxide films deposited at oxygen fractions (a) $\Gamma=0.5$ and (b) 0.6 after exposure to air for 30 days.

XRR, described in detail by Ferrari et al. [166], was utilized to calculate the density of the rhenium oxide films after 1 day and 30 days of atmospheric exposure. Due to the high levels of macro-segregation, and the resulting non-uniform surface morphology, XRR analysis was limited to the calculation of density by measurement of
the total reflection, or critical angle [166]. Films deposited at $\Gamma=0.6$ were shown to retain their initial density of 5.2 g/cm$^3$, while films deposited at $\Gamma=0.5$ showed an average density reduction from 5.0 to 3.8 g/cm$^3$. Measured density values range from 5.3-3.6 g/cm$^3$, while typical densities for rhenium oxides ranged from 11.4 g/cm$^3$ for ReO$_2$ to 6.10 g/cm$^3$ for Re$_2$O$_7$ [18,156]. Density values far below the relatively low density of Re$_2$O$_7$ are indicative of the presence of much lower density HReO$_4$. Thickness measurements via SE for $\Gamma=0.5$ indicate thickness changes from 80 (±10) nm in vacuo to 150 (± 20) nm, after 30 days air exposure. Films deposited at $\Gamma=0.6$ were 90 (± 7) nm thick in vacuo and 93 (± 7) nm after 30 days air exposure. Despite microstructural non-uniformity, thickness changes measured using ellipsometry correlate to volumetric expansion related to density reduction after 30 days.

5.3.3 Surface analysis

The composition and chemical state of the rhenium oxide films, measured using XPS, demonstrated marked changes as a result of environmental exposure. Survey (Figure 28) and high-resolution (Figure 29) scans were acquired for films deposited at $\Gamma=0.5$ and 0.6 after exposure to air for 1 and 30 days. The survey scan of the film deposited at $\Gamma=0.5$ after 1 day of exposure showed a composition of 30% Re, and 70% O, with negligible amounts of adventitious carbon. After 30 days of exposure, the $\Gamma=0.5$ film was found to have a surface composition of 25% Re, 64% O, and 11% C. The compositions of rhenium oxide deposited at $\Gamma=0.6$, following air exposures of 1 and 30 days changed from 30 to 27% Re, 70 to 65% O, and 0 to 8% C, respectively.
Figure 28. XPS survey scans used for composition measurement for films deposited at $\Gamma=0.5$ and 0.6 after 1 day air exposure. Spectra are offset for clarity.

Figure 29. High resolution XPS spectra of the Re 4f transition for films deposited at (a) $\Gamma=0.5$ and (b) 0.6. Spectra are offset for clarity.
High resolution XPS (Figure 29), performed after 1 day of air exposure, indicated that all films deposited were found to contain 4f transitions with binding energies corresponding to valence states of Re$^{4+}$, Re$^{6+}$, Re$^{7+}$, for their respective compounds: ReO$_2$, ReO$_3$, and Re$_2$O$_7$ [66,154,167]. In addition to the aforementioned compounds, films deposited at $\Gamma=0.5$ were found to contain up to 15% of the Re$^{3+}$ valence state. The presence of the Re$^{3+}$ valence state, and its corresponding oxide, Re$_2$O$_3$, has been reported previously in the literature [158,164,168,169]. Interestingly, Re$_2$O$_3$ has been reported to undergo catalytic disproportionation in the presence of moisture, decomposing into metallic Re$^0$ and hydrous ReO$_2$, as described in Equation 15 [158,168,169]:

$$2\text{Re}_2\text{O}_3 + 6\text{H}_2\text{O} \rightarrow \text{Re}^0 + 3(\text{ReO}_2\cdot2\text{H}_2\text{O})$$ (15)

Binding energies corresponding to the Re 4f$_{7/2}$ transitions are shown in Table 10. The chemical state distribution measured for $\Gamma=0.5$ (Figure 29a) after 1 day air exposure consists of 15% Re$^{3+}$, 10% Re$^{4+}$, 55% Re$^{6+}$, and 20% Re$^{7+}$.

Table 10. Re 4f$_{7/2}$ binding energies measured from curve fitted data for $\Gamma = 0.5$ and 0.6.

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>$\Gamma=0.5$</th>
<th>$\Gamma=0.6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3+</td>
<td>42.4</td>
<td>--</td>
</tr>
<tr>
<td>4+</td>
<td>42.9</td>
<td>42.9</td>
</tr>
<tr>
<td>6+</td>
<td>44.9</td>
<td>44.9</td>
</tr>
<tr>
<td>7+</td>
<td>46.4</td>
<td>46.9</td>
</tr>
</tbody>
</table>

After air exposure for t=30 days (Figure 29a), the surface chemistry is 7% Re$^{3+}$, 5% Re$^{4+}$, 88% Re$^{6+}$, and 0% Re$^{7+}$. Given the reported instability of both Re$_2$O$_3$ and Re$_2$O$_7$ in the presence of moisture [18,26,61,154,156,158], it is possible that both hydrous ReO$_2$ and liquid HReO$_4$, could have formed during environmental exposure and subsequently
evaporated under the UHV conditions within the XPS instrument. Tysoe et al., have reported similar losses of rhenium species, correlated to the presence of Re$_2$O$_7$ [154]. Films deposited at $\Gamma=0.6$ (Figure 28b) were found to contain 40% Re$^{4+}$, 53% Re$^{6+}$, and 7% Re$^{7+}$ after 1 day, and 40% Re$^{4+}$, 50% Re$^{6+}$, and 10% Re$^{7+}$ after 30 days, exhibiting very little change as a result of environmental exposure. Therefore, according to the XPS results, the surface chemistry of films grown at $\Gamma=0.6$ remained relatively stable, while films grown at $\Gamma=0.5$ demonstrated large changes after 30 days air exposure.

Given the uncertainty inherent in the peak fitting process, comparisons were made between high energy resolution data obtained for films deposited at $\Gamma=0.5$ and 0.6, and those analyzed within the literature [158,164,167,170]. In addition to probing the accuracy of the fitting process, the comparisons shown in Figure 30 help to identify potential trends in peak location as a function of oxidation state. Identification of known binding energy shifts is especially helpful for the validation of the presence of the unstable Re$^{3+}$ oxidation state. Typically, as a result of increases in binding energy brought on by oxygen bonding, the binding energy will increase linearly as a function of oxidation number. In this case, the binding energy shifts attributed to the Re$^{3+}$, Re$^{4+}$, Re$^{6+}$, and Re$^{7+}$ states are approximately linear with respect to each other, but do not intersect with the point established for Re$^0$. This observed trend has been noted elsewhere by Komiyama et al. [164]. The locations of Re 4f$_{7/2}$ peaks obtained within this study are in agreement with reported values.
Figure 30. Plot of the binding energy shift for the Re 4f$_{7/2}$ peak as a function of oxidation state, as compared to results obtained by Liu et al [170], Cimino et al. [167], Tysoe et al. [154], Shpiro et al. [171], and Komiyama et al [164].

5.3.4 Optical properties

Detailed spectroscopic ellipsometry analysis of the rhenium oxide thin films was conducted in vacuo for films grown at $\Gamma$=0.5 and 0.6. The measurements were made over a wavelength range of 380 to 1700 nm. The resulting magnitude ($\psi$) and phase difference ($\Delta$) information obtained from the two samples was then parameterized using two Lorentz oscillator models, as described elsewhere by Jellison [172]. Multiple oscillators were required due to the fact that ReO$_3$ facilitates absorption via interband transitions at $\lambda<540$ nm ($h\nu > 2.3$ eV) specifically the tail of the absorption feature centered at 310 nm (4 eV) as the other interband absorption features are out of the range of the ellipsometer used for these measurements. Additional absorption features accounted for within the
model include free-electron, or intraband transitions beginning at \(\lambda=540\) nm and increasing into the NIR and IR \((h\nu < 2.3\) eV\) [27,28,158,160]. Oscillator parameters, error estimates, and goodness-of-fit data can be found in Table 11. Figure 31a shows both the refractive index and extinction coefficient values at different exposure times.

Table 11. General oscillator parameters and error estimates used for fitting ellipsometry data.

<table>
<thead>
<tr>
<th>(\Gamma)</th>
<th>t (days)</th>
<th>Amplitude</th>
<th>Broadening</th>
<th>Center energy (eV)</th>
<th>d (nm)</th>
<th>MSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0</td>
<td>3.3 ± 0.3</td>
<td>0.54 ± 0.01</td>
<td>3.42 ± 0.01</td>
<td>79</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.8 ± 0.9</td>
<td>3.76 ± 0.05</td>
<td>0.70 ± 0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3.3 ± 0.1</td>
<td>0.54 ± 0.01</td>
<td>3.42 ± 0.01</td>
<td>79</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.9 ± 0.9</td>
<td>3.77 ± 0.04</td>
<td>0.71 ± 0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.42 ± 0.02</td>
<td>0.45 ± 0.03</td>
<td>2.80 ± 0.01</td>
<td>150</td>
<td>15.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.15 ± 0.01</td>
<td>1.25 ± 0.01</td>
<td>1.68 ± 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>12 ± 1</td>
<td>0.44 ± 0.04</td>
<td>4.5 ± 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>0</td>
<td>35 ± 1</td>
<td>0.85 ± 0.01</td>
<td>0.58 ± 0.01</td>
<td>90</td>
<td>8.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.8 ± 0.1</td>
<td>0.53 ± 0.01</td>
<td>3.30 ± 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>28 ± 0.9</td>
<td>0.91 ± 0.01</td>
<td>0.63 ± 0.01</td>
<td>89</td>
<td>10.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.8 ± 0.1</td>
<td>0.53 ± 0.01</td>
<td>3.33 ± 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>39 ± 2</td>
<td>0.73 ± 0.01</td>
<td>0.64 ± 0.01</td>
<td>93</td>
<td>22.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.9 ± 0.1</td>
<td>0.49 ± 0.02</td>
<td>3.27 ± 0.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 31. Optical constants (n, k) obtained for mixed valent rhenium oxide thin films (a) from 380-1700 nm. Note that both refractive index and extinction coefficient values for films deposited at $\Gamma=0.5$ in vacuo (thin dashed) and after 1 day exposure (dotted) overlap one another significantly. The 30 day data within the dashed boxes in part (a) are expanded and shown within part (b), along with comparisons to reported values by Feinleib et al. [12], Weaver et al. [13], Ghanashyam Krishna et al. [4] and Hahn et al. [6].

For $\Gamma=0.6$, initial and prolonged exposure to atmosphere have very little effect on the optical properties. Free electron absorption within the near infrared region is parameterized using a Lorentz oscillator centered at 1940 nm (0.64 eV) the corresponding extinction coefficients and refractive indices are shown to increase.
alongside wavelength, as expected in the case of intraband transitions [80]. Interband transitions, occurring at 375 nm (3.3 eV), are close to the known ReO₃ absorption band at 310 nm (4.0 eV); discrepancies between these two values are likely due to the fact that the ellipsometer is not equipped to go below 380 nm (above 3.25 eV). Note that ReO₃ undergoes additional interband transitions at 177, 155, 124 and 89 nm (7, 8, 10 and 14 eV) [27,28,160], while Re₂O₇ has absorption bands at 310 and 240 nm (4.0 and 5.2 eV) [27,63]. Therefore, it will be difficult to determine if absorption occurring at or near 310 nm (4 eV) is characteristic of either compound. In the case of films deposited at \( \Gamma = 0.5 \), the initial optical behavior is similar to that of the \( \Gamma = 0.6 \) films, experiencing interband transitions near 375 nm (3.3 eV), with intraband absorption occurring above 540 nm (2.3 eV), centered at 1900 nm (0.65 eV). Films deposited at \( \Gamma = 0.5 \) demonstrate little change upon initial exposure to atmosphere, however, the optical properties are shown to have rapidly degraded after 30 days air exposure. These films no longer demonstrate the characteristic free electron absorption associated with ReO₃, instead they have a very low extinction coefficient, less than 0.7 from 380 to 1700 nm. In addition, the \( \Gamma = 0.5 \) film required three Lorentz oscillators to accommodate absorption bands at 443, 752 and 295 nm (2.8, 1.65 and 4.2 eV). These films demonstrate similar optical behavior to highly oxidized, solution deposited rhenium oxide compounds obtained by Hahn et al. [158] as shown in Figure 31. Additional comparisons between films deposited at \( \Gamma = 0.6 \) and results obtained by Feinleib et al. [28] and Weaver et al. [160], for single crystal ReO₃, can be seen in Figure 31b, where our data indicates reasonably similar optical behavior to their bulk single crystals.
5.4 Conclusions

Despite having only a 10% percent difference in $\Gamma$ values, rhenium oxide films deposited at $\Gamma=0.5$ and 0.6 have disparate optical and chemical properties, especially as a function of environmental exposure time. While films deposited under both conditions are composed of similar proportions of rhenium to oxygen, 70% O and 30% Re, as calculated via XPS, their chemistries are quite different. The main difference between the oxide species present in films deposited at $\Gamma=0.5$ and 0.6 is the existence of Re$^{3+}$ associated with an oxygen fraction of 0.5. Films containing the Re$^{3+}$ valence state, a result of the lower oxygen fraction used during growth, have demonstrated large decreases in density, droplet formation, poor adhesion, and rapid degradation of optical performance. Similarly, films deposited at $\Gamma=0.6$ have shown poor adhesion, and slight microstructural instability in the form of compressive-mode cracking. However, films deposited at $\Gamma=0.6$ possess very small changes in their optical and chemical properties as a function of environmental exposure. The poor adhesion and microstructural instability of the mixed valent rhenium oxide films within this study are consistent with other reports of moisture related degradation. Despite the structural implications associated with exposure to moisture, films deposited at an oxygen level sufficient to preclude the formation of Re$^{3+}$ were able to retain their optical and chemical properties throughout the 30 day exposure period.
6. HYBRID CO-DEPOSITION AND CHARACTERIZATION OF MIXED-VALENT MOLYBDENUM-GERMANIUM OXIDE (MoₓGeᵧO₂) FILMS

6.1 Introduction

Multi-component oxide thin films have found uses in several applications spanning the fields of optics and electronics. Some examples of the multitude of uses for these materials include transparent conductive oxides (TCOs), such as aluminum zinc oxide (AZO) [173-175] and indium tin oxide (ITO) [175-177], switchable electrochromic smart windows [29,151,178-181], flat panel displays [182-185], and optical coating designs requiring mixtures of high and low refractive index materials, such as rugate filters [186,187] and infrared reflectors [173]. While most of these applications require fully stoichiometric, transparent oxide mixtures, recent works exploring sub-stoichiometric oxide systems have generated interest due to their unique absorptive properties [15-17]. Specifically, studies by Gil-Rostra et al. [15,17,188,189] have utilized reactive magnetron sputtering to tailor the visible absorption of substoichiometric transition metal oxides, including Ni [15], Co [15,189], Fe [15], Cu [15,188], W [15,17], and Mo [15], within a dielectric silicon dioxide matrix. Gil-Rostra et al. were able to deposit a variety of colorful “ionic glass” thin films by varying the fraction, and chemistry, of transition metal cations within the SiO₂ matrix [15,190-192]. Specifically, the visible absorption characteristics associated with transition metal coordination complexes, perceived as color by the human eye, are attributed to the splitting of d-electron energy levels as a result of metal-ligand bonding [193,194]. The ability to
systematically leverage the visible absorption of thin film coatings has several advantages for the development of coatings for ophthalmic usage [17,188,189,195], photovoltaics [37,129,176,179,196], LED components [197-199], and plasmonics, providing a potential alternative to lossy metal-based configurations [200-203].

To properly facilitate sputter deposition of mixed-valent ionic glasses, two distinct materials must be selected. Materials required include a stable, dielectric matrix, as well as an easily reducible transition metal oxide. Typically, the selection of the metallic species is limited to those transition metals and lanthanides that have unfilled d and f electron shells, respectively, which give rise to visible absorption as a result of excitation energies ranging from ~1 to 3 eV (λ ≈ 400-1240 nm) [193,194,204]. Given that these materials will be deposited simultaneously, it is also necessary that the intended matrix phase is able to form a fully stoichiometric oxide, without also leading to full oxidation of the absorbing constituents, potentially rendering them transparent to visible wavelengths. The likelihood of disparate materials bonding to form coordination compounds, transparent or otherwise, is governed by the enthalpy of formation, which represents the thermodynamic driving force for reactivity. The Ge-O and Mo-O systems are of interest due to the fact that the enthalpies of formation of substoichiometric MoO2 (relative to MoO3) and stoichiometric GeO2 are very similar at room temperature, ΔfH°(MoO2) = -588 kJ/mol and ΔfH°(GeO2) = -580 kJ/mol [18], a potential indicator that these two compounds can be deposited concurrently. In addition to MoO2 (Mo4+), the facile reduction of MoO3 can lead to the formation of Mo2O5, and the corresponding ionic species, Mo5+ [116-118]. Therefore, it should be possible to control the relative amounts
of absorptive, substoichiometric MoO$_x$ (0<x<3) coordination compounds within a transparent GeO$_2$ matrix.

Several methods employing reactive magnetron sputtering have been studied for depositing both stoichiometric and substoichiometric mixed oxide thin films. Methods used for successfully depositing mixed oxides include the use of alloyed targets [205-209], affixing strips of various materials to the target surface [15,17,188,189], and co-deposition using multiple sources [210-213]. While each of these methods is capable of depositing uniform, high quality thin films, co-deposition was selected for use within this study. Justification for the use of co-deposition is due to the dynamic experimental environment associated with the use of two separate magnetron sources, allowing for independent variation of power application, magnet configuration, working distance, and target diameter. Unlike previous studies of co-deposited mixed oxide systems, this study utilizes an ionized physical vapor deposition technique known as modulated pulse power magnetron sputtering (MPPMS). MPPMS was used due to its ability to generate high target power densities, allowing for rapid reduction of oxygen on the surface of the “oxygen poisoned” molybdenum cathode, as well as for its highly metallic plasma resulting in increased oxygen-gettering capability [2,4,136,144]. Therefore, fine adjustments in the applied MPPMS power should be able to accurately control the oxygen partial pressure within the deposition chamber via chemisorption [3,4,19,83,84].

This work uses a scalable co-deposition method that allows the precise control of oxygen partial pressure in order to achieve controlled variation in both the composition and chemical state of mixed Mo$_x$Ge$_y$O$_z$ thin films. This work also explores the reduction pathway of the oxides present within the deposited films, and provides a detailed
correlation between processing parameters, chemical properties, and optical behavior. Given the large number of variables associated with reactive co-sputtering (Section 2.6), the correlation between oxygen partial pressure and average film valence state is explored, and validated, using a modified version of the Berg model [83]. Finally, the methods outlined within this study are intended to serve as a template for the deposition and characterization of other substoichiometric mixed-oxide systems.

6.2 Experimental

6.2.1 Fabrication

$\text{Mo}_x\text{Ge}_y\text{O}_z$ films were deposited within the stainless steel high-vacuum chamber (as described within Section 2.1) equipped with two diametrically opposed magnetron sources aligned in a confocal arrangement. Two unbalanced, 50 mm diameter magnetron sources with equivalent magnetic field strengths were used in this work. The first magnetron (K.J. Lesker Torus) was equipped with a 50 mm germanium (Plasmatic, 99.999% purity) sputter target. The second magnetron (Meivac MAK) was equipped with a 50 mm molybdenum target (Plasmatic, 99.95%). Both magnetrons were positioned at a 20° angle with respect to the substrate normal. Substrates, both prime grade (001) p-type silicon (University Wafer LLC) and fused quartz (Machine Glass Specialists Inc.) were loaded into the chamber through a load-lock system. Substrates were placed on an unheated holder set to rotate at 12 rpm to reduce anisotropy imparted by the sputtering process. The position of the magnetrons was set to ensure a target-to-substrate distance of 13 cm. All substrates were covered with a shutter to shield against spurious droplets at the onset of sputtering.
Prior to plasma ignition, the chamber was evacuated to a pressure of $6.6 \times 10^{-5}$ Pa ($5.0 \times 10^{-7}$ Torr), or better, using a turbomolecular pump in conjunction with a mechanical roughing pump. Upon achieving the required base pressure, argon (99.999%) was introduced into the vacuum chamber at a flow rate ($Q_{Ar}$) of 25 sccm using a mass flow controller. The pressure of the argon gas ($P_{Ar}$), measured using a capacitance manometer, was set at 1.33 Pa (10 mTorr) and maintained constant by locking the gate valve position. The static gate valve resulted in a constant pumping speed of approximately 32 L/s. $P_{Ar}$ was expected to be constant throughout all depositions, assuming a negligible amount of argon loss through ion implantation at the target surfaces. Once $P_{Ar}$ was stabilized at 1.33 Pa (10 mTorr), oxygen (99.995%) was introduced through a separate mass flow controller. The oxygen partial pressure, $P_{O2}$, was determined by subtracting $P_{Ar}$ from the total chamber working pressure $P_{TOT}$. The oxygen flow rate ($Q_{O2}$) was first stepped from 0 to 10 sccm, in 1 sccm increments. Adjustment of $Q_{O2}$ took place in order to determine the onset of the “poisoned” regime, ensuring sufficient oxygen levels to correspond to fully oxidized films. The value of $Q_{O2}$ was set to 6 sccm resulting in a total flow rate ($Q_{TOT}$) of 31 sccm. Justification for the selection of $Q_{O2}$ can be found in section 6.3. Note that the gases were not mixed prior to entering the chamber. Oxygen was introduced through a port near the substrate holder, while argon was introduced near the top of the chamber, in the vicinity of the magnetron sources.

The plasma was generated using two separate power supplies; an Advanced Energy MDX 500 power supply was used for the germanium source, while a ZPulser Axia 180 modulated pulse power supply was used for the molybdenum source. Germanium sputtering took place at a constant power of 100 W, and molybdenum
deposition via MPPMS was carried out with specific capacitor bank voltages ($U_c$) that were systematically varied from 0 to 380 V. MPPMS discharge events, lasting 1 ms at a frequency of 100 Hz, resulted in a duty cycle of 10%. The 1 ms pulse was separated into two different regimes, similar to the pulse profiles used by Hála et al. [4]. The first stage of the pulse generated a low energy plasma discharge with a duration of 400 μs derived from a 20% micropulse duty cycle, and the second stage consisted of a higher energy plasma lasting 600 μs controlled by micropulses applied at a 54.5% duty cycle with an on time of 12 μs and an off time of 10 μs. Temporal voltage and current output were monitored using a Tektronix DPO 5204 multi-channel oscilloscope. Films were deposited on 50 mm diameter silicon substrates and 25 mm diameter fused quartz witness samples for a total of three minutes, resulting in thicknesses ranging from 220 to 300 nm. In the case of samples prepared for x-ray reflectivity, the deposition time was held to one minute to ensure an appropriate thickness ($\leq$ 100 nm).

6.2.2 Characterization

The composition, chemistry, optical properties, and structure of as deposited Mo$_x$Ge$_y$O$_z$ thin films were studied using a combination of grazing incidence x-ray diffraction (GIXRD), x-ray reflectivity (XRR), x-ray photoelectron spectroscopy (XPS), in situ and ex situ spectroscopic ellipsometry (iSE, SE), and ultraviolet-visible-near-infrared optical spectrophotometry (UV-Vis-NIR).

Structural properties of the as-deposited Mo$_x$Ge$_y$O$_z$ films, including roughness, thickness, crystallinity, and density, were measured using GIXRD and XRR. Both GIXRD and XRR measurements were performed with a Rigaku SmartLab x-ray diffractometer using a Cu-Kα (1.5418 Å) source. GIXRD measurements were taken
within a 2θ range of 15-80º at a rate of 0.1º/s. XRR scans were obtained for 2θ values between 0.0º and 6.0º with a step size of 0.005º. Raw XRR data were fit in the Rigaku Globalfit software package.

XPS analysis was used to measure both the composition and chemical valence states of the compounds present in the films. XPS measurements were performed using a Physical Electronics 5700 equipped with a monochromatic Al Kα (1486.6 eV) x-ray source. Compositional analysis took place using survey scans at an analyzer pass energy of 187.85 eV from 0 to 1400 eV binding energy, while an analyzer pass energy of 29.35 eV was used for high energy resolution measurements to determine the chemical valence states of the deposited species. For convenience, all spectra were calibrated with respect to the adventitious carbon 1s transition at a binding energy (BE) of 284.6 eV. High energy resolution scans were fit with Gaussian-Lorentzian line shapes after Shirley background subtraction. Processing of XPS spectra was performed using the CasaXPS 2.3.16 software package [82].

The optical properties of the MoₓGeᵧO₂ films were evaluated using iSE, SE and UV-VIS-NIR spectrophotometry. SE and iSE measurements were taken using a J.A. Woollam M2000VI spectroscopic ellipsometer operating at a wavelength range of 380-1700 nm. Raw ellipsometry data is gathered by monitoring the changes in both the magnitude (Ψ) and phase difference (Δ) of polarized light after interaction with the sample surface. The spectral refractive index (n(λ)), the extinction coefficient (k(λ)) and the thickness of the films were calculated by fitting raw SE and iSE data with a Kramers-Kronig consistent optical model, described in detail in section 6.3. Note that the optical model was fit to the raw Ψ and Δ data, and optimized in order to minimize the resulting
mean squared error (MSE). The model’s MSE values were reduced through iterative adjustment of the fitting parameters using the Levenberg-Marquardt method, improving the fit quality [214]. Models with an MSE greater than 18 were rejected. Optical transmission and reflectivity data were measured with a Perkin-Elmer Lambda 1050 UV-VIS-NIR spectrophotometer with an integrating sphere attachment. Reflectivity and transmission values were used for calculation of the absorption coefficient ($\alpha$). Multiple Tauc plots were then constructed in order to determine the magnitude of the optical gap, $E_g$.

6.3 Results and discussion

6.3.1 Establishment of Conditions

The oxygen partial pressure ($P_{O_2}$), as a function of flow rate ($Q_{O_2}$), was carefully monitored prior to deposition with both magnetron sources. As mentioned previously, the partial pressure of argon ($P_{Ar}$) was set to 1.33 Pa (10 mTorr) and then oxygen was introduced into the deposition chamber. Pumping speeds were calculated by analyzing the working pressure as a function of $Q_{O_2}$ prior to plasma ignition in order to ensure there was no reduction in $P_{O_2}$ through oxide formation due to chemisorption.

Using only the Ge source, a plot of ($P_{O_2}$) versus $Q_{O_2}$ is shown in Figure 32. The pumping speed ($S=Q_{TOT}/P_{TOT}$) attributed to each set of $P_{TOT}$ vs. $Q_{TOT}$ was calculated, resulting in an average rate of 32 L/s. $P_{TOT}$ was then evaluated as a function of $Q_{O_2}$ with the germanium source operating at 100 W DC, in order to establish the locations of the gettering, transition, and poisoned regimes associated with the reactive sputtering process for Ge [2,3,137,141]. As demonstrated in Figure 32, the value of $P_{O_2}$ at $Q_{O_2}=0.0$ is 0 Pa, validating the assumption of constant argon pressure during sputtering. As $Q_{O_2}$ increases
to 1 sccm, there is no change in $P_{O_2}$, indicating that all available oxygen is effectively chemisorbed by the sputtered germanium. Changes in $P_{O_2}$, associated with the presence of gaseous oxygen, begin to arise at $Q_{O_2} \geq 2$ sccm. Increases in $P_{O_2}$ for $1 < Q_{O_2} \leq 5$ sccm signify the onset of the transition regime, wherein the germanium deposition flux is unable to fully react with the available oxygen, leading to the gradual oxidation of the target, substrate, and adjacent surfaces. Note the mild hysteresis occurring within the transition region in Figure 32, this commonly reported behavior is associated with the oxidation and reduction of the sputter target surface as reactive gas content is varied [3,83,84,137,138,141]. At $Q_{O_2}$ values near 5 sccm and above, $P_{O_2}$ increases linearly at a rate proportional to the pumping speed of the system. The linear behavior of $P_{O_2}$ above 5 sccm can be attributed to the saturation of both the Ge target and collecting surfaces with chemisorbed oxygen; therefore, excess oxygen can only be removed through the pumping system. The identification of the onset of the poisoned regime for Ge is associated with the formation of fully stoichiometric GeO$_2$.

The establishment of conditions using the Ge target was also used to validate the single target Berg model and establish the total pumping speed ($S$) including decreases in $P_{O_2}$ due to chemisorption associated with the deposition flux. As shown in Figure 32, the Berg model depicting the response of $P_{O_2}$ as a function of $Q_{O_2}$ at $S=37.5$ L/s is in good agreement with the experimental results, accurately predicting the onset of the gettering, transition, and poisoned sputtering modes. Note that the experimentally measured $S$ is 32 L/s; the difference between the measured and calculated $S$ values is likely the result of changes in ambient temperature and oxygen chemisorption associated with the deposition
flux. After validation of the single target system, the Berg model was then adapted to the two-target system.

The goal of this work requires the initial deposition of transparent, dielectric GeO₂ and MoO₃, followed by the incorporation of optically absorbing metal-oxide coordination complexes associated with sub-stoichiometric oxide formation characteristic of transition mode sputtering [3,83,84,137,138,141]. Therefore, deposition of mixed-valent molybdenum and germanium oxides must take place within the transition regime, leveraging the high metallic target flux associated with the MPP process to control the oxygen partial pressure, and subsequently, the composition and chemistry of the deposited films [4,19,215].

![Graph](image)

Figure 32. Oxygen partial pressure (P₀₂) as a function of oxygen flow rate (Q₀₂) for increasing (red triangles) and decreasing (blue triangles) oxygen flow rates for sputtering from a Ge target. Note that the pressure was also measured as a function of flow rate under ambient conditions (black squares).
Having identified and accurately modeled the onset of target poisoning for germanium deposition, characterization of the $P_{O_2}$ vs. $Q_{O_2}$ behavior for the co-deposition from Ge and Mo targets was performed using $Q_{O_2}$ values of 4, 6, and 8 sccm. $P_{TOT}$ values corresponding to $Q_{O_2}$ values of 4, 6, and 8 sccm were recorded as a function of $U_c$ applied to the molybdenum sputter source; note that the germanium source was operated concurrently at 100 W DC. A plot of $P_{O_2}$ vs. $U_c$, shown in Figure 33, demonstrates significant differences in behavior for $Q_{O_2}$ values of 4, 6, and 8 sccm. Based on the data in Figure 33, the onset of the transition regime is demonstrated by the characteristic decrease in $P_{O_2}$ as a function of increasing $U_c$.

The relatively flat behavior of $P_{O_2}$ at lower $U_c$ values is attributed to the inability to fully react with the excess oxygen present within the chamber, consistent with the poisoned regime. As $U_c$ increases, the pressure begins to decrease due to the higher levels of molybdenum deposition flux brought on by the augmentation of $U_c$. Since $U_c$ is directly related to the magnitude of the discharge voltage, depicted in Figure 35a, increases in $U_c$ are responsible for augmenting the kinetic energy of incident $Ar^+$ ions responsible for sputtering. Therefore, further increases in $U_c$ lead the reduction of oxides formed on the target surfaces, giving way to the onset of transition mode sputtering, as demonstrated by the decrease in $P_{O_2}$ and $P_{TOT}$. As shown in Figure 35a, the slope of the voltage discharge at $t > 1$ ms begins to increase as the target surface becomes more metallic. The gettering regime is easily identified due to the fact that all oxygen present within the chamber is chemisorbed by the adatoms from the deposition flux, therefore there will be a net $P_{O_2}$ of 0.00 Pa, corresponding to $P_{Ar}=1.33$ Pa. The onset of gettering is clear for $Q_{O_2}=4$ sccm, at 330 V (Figure 33), while $Q_{O_2}$ values of 6 and 8 sccm correspond
to $P_{O_2}$ levels that are unable to be fully chemisorbed by the deposition flux even at $U_c=380$ V. The resulting augmentation of the molybdenum deposition flux is associated with both an increase in both discharge current (Figure 35b) and photoemission attributed to excited molybdenum species (Mo I) (Figure 35c). Current and voltage values for the Ge and Mo sputter sources can be found in Table 12 and Table 13, respectively. Note, the $U_c$ value of 380 V corresponds to an average current of approximately 0.7 A; higher $U_c$ settings could not be used due to the thermal constraints of the magnetrons. The levels of $P_{O_2}$ for $Q_{O_2}=6$ sccm, are shown to have sufficient sensitivity to $U_c$ to allow for reduction of the oxygen content in the chamber, while still retaining stability over a wide range of partial pressures (Figure 33). As a result of this analysis, $Q_{O_2}=6$ sccm was selected for the deposition of $Mo_xGe_yO_z$ films. The two-target Berg model was then used to calculate the response of $P_{O_2}$ ($Q_{O_2}=6$ sccm) under conditions corresponding to changes in $U_c$, as shown in Figure 34. As shown in Figure 34, the behavior of $P_{O_2}$ is well predicted by the two target Berg model. The Berg model calculation of $P_{O_2}$, as a function of $U_c$, validates the initial assumption that changes in $U_c$ allow for precise adjustment in $P_{O_2}$. Since $P_{O_2}$ represents the amount of oxygen available for compound formation, it is possible to utilize the Berg Model to calculate the average valence states of each individual compound within the films as a function of the processing parameters, as discussed in Section 2.6.
Figure 33. Plot of oxygen partial pressure ($P_{O_2}$) as a function of MPP capacitor bank voltage ($U_c$).

Figure 34. Comparison of measured and calculated oxygen partial pressures, at $Q_{O_2}=6$ sccm, as a function of capacitor bank voltage ($U_c$).
Figure 35. Temporal evolution of (a) voltage and (b) current associated with the molybdenum cathode during the MPPMS pulse. Photoemission events attributed to the excited molybdenum (Mo I) are shown in (c). Spectra are offset for clarity.
Table 12. DC voltage, current, and power output of germanium sputter source in response to changes in $U_c$ applied to the molybdenum cathode during co-deposition.

<table>
<thead>
<tr>
<th>$U_c$ (V)</th>
<th>DCMS Germanium</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Voltage (V)</td>
<td>Current (I)</td>
<td>Power (W)</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>520</td>
<td>0.190</td>
<td>98.8</td>
<td></td>
</tr>
<tr>
<td>310</td>
<td>523</td>
<td>0.190</td>
<td>99.4</td>
<td></td>
</tr>
<tr>
<td>320</td>
<td>522</td>
<td>0.190</td>
<td>99.2</td>
<td></td>
</tr>
<tr>
<td>330</td>
<td>522</td>
<td>0.190</td>
<td>99.2</td>
<td></td>
</tr>
<tr>
<td>340</td>
<td>519</td>
<td>0.190</td>
<td>98.6</td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>516</td>
<td>0.190</td>
<td>98.0</td>
<td></td>
</tr>
<tr>
<td>360</td>
<td>513</td>
<td>0.192</td>
<td>98.5</td>
<td></td>
</tr>
<tr>
<td>370</td>
<td>513</td>
<td>0.193</td>
<td>99.0</td>
<td></td>
</tr>
<tr>
<td>375</td>
<td>511</td>
<td>0.194</td>
<td>99.1</td>
<td></td>
</tr>
<tr>
<td>380</td>
<td>506</td>
<td>0.196</td>
<td>99.2</td>
<td></td>
</tr>
</tbody>
</table>

Table 13. DC voltage, current, and power output of molybdenum sputter source as a function of $U_c$.

<table>
<thead>
<tr>
<th>$U_c$ (V)</th>
<th>MPPMS Molybdenum</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak Voltage (V)</td>
<td>Peak Current (I)</td>
<td>Peak Power (W)</td>
<td>Average Voltage (V)</td>
<td>Average Current (I)</td>
<td>Average Power (W)</td>
</tr>
<tr>
<td>300</td>
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<td>0.441</td>
<td>270.5</td>
<td>524</td>
<td>0.261</td>
<td>136.9</td>
</tr>
<tr>
<td>310</td>
<td>632</td>
<td>0.446</td>
<td>282.1</td>
<td>536</td>
<td>0.265</td>
<td>142.1</td>
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<tr>
<td>320</td>
<td>649</td>
<td>0.522</td>
<td>338.6</td>
<td>546</td>
<td>0.283</td>
<td>154.4</td>
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<tr>
<td>330</td>
<td>669</td>
<td>0.581</td>
<td>388.9</td>
<td>555</td>
<td>0.298</td>
<td>165.6</td>
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<td>340</td>
<td>685</td>
<td>0.683</td>
<td>468.3</td>
<td>562</td>
<td>0.333</td>
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</tr>
<tr>
<td>350</td>
<td>705</td>
<td>0.903</td>
<td>636.9</td>
<td>566</td>
<td>0.374</td>
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<td>563</td>
<td>0.406</td>
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<tr>
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<td>0.471</td>
<td>261.8</td>
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<td>1213.4</td>
<td>546</td>
<td>0.518</td>
<td>283.3</td>
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<tr>
<td>380</td>
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<td>2.825</td>
<td>2055.5</td>
<td>494</td>
<td>0.712</td>
<td>351.4</td>
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100
6.3.2 Structure and morphology

Measurement of the crystallinity of Mo₅Ge₇O₂ thin films indicated that all films deposited were amorphous, as evinced by the presence of the lack of diffraction peaks in XRD, as well as the broad amorphous humps shown in Figure 36. Similar amorphous character has been reported by Mohamed et al. for sputter deposited MoO₃, demonstrating broad amorphous humps with centroids moving from 2θ=27º to 2θ=38º as the oxygen partial pressure is decreased from 0.16 to 0.022 Pa [36]. The lack of long-range structural order within these films can be attributed to low adatom mobility related to the low deposition temperature (T ≤ 100°C), interruption of film nucleation via the formation of a surface coating layer [13,153,216], and incompatibility of mixing between the germanium and molybdenum oxide compounds [217,218]. The amorphous structure of multi-component oxide coatings deposited at room temperature has also been reported by Gil-Rostra et al. for a variety of mixed-valent films [15,17,188,189].

XRR measurements were performed to probe the density, thickness, and roughness of the Mo₅Ge₇O₂ films deposited at Uᵢ values of 300 to 380 V. XRR is able to provide in estimation of the density based on the location of the critical angle (θᵦ), below which, the total reflection of incident x-rays occurs [219]. In addition to density, film thickness can be calculated based on the period of oscillations known as Kiessig fringes [219]. Finally, surface and interface roughness values can be determined as a function of the decay in x-ray signal, attributed to scattering losses at increasing values of 2θ [219]. The model used for XRR fitting and calculation consisted of a silicon substrate with a 2 nm native SiO₂ layer, an interfacial roughness layer, and finally a homogeneous layer of unconstrained density, thickness and surface roughness. The assumption of a
homogeneous film microstructure, consisting of a random solid solution of metallic
cations within a germanium oxide matrix, is based upon reports by Gil-Rostra et al. for
similar mixed oxide systems [15,17,188,189]. Based on the data shown in Figure 37, the
behavior of the reflected x-ray intensity shows an increase in $\theta_c$ with increasing capacitor
bank voltage, indicating densification as a function of increasing voltage. Simulated XRR
spectra indicate good agreement between experimentally obtained values and model
assumptions, as shown in Figure 37. Roughness values remained relatively stable as a
function of $U_c$, varying between 1.5 and 2.0 nm, while calculated densities (Figure 38)
demonstrate a non-linear increase as a function of $U_c$. Note that the calculated density
rises from 3.2 to 6.4 g/cm$^3$ as $U_c$ is increased from 300 to 380 V. The initial low density
values, at $300 \leq U_c \leq 350$ can be attributed to the relatively high amount of residual
oxygen present within the chamber (Figure 33), resulting in the growth of fully oxidized
films. However, the densities of the oxygen-rich films within the $300 \leq U_c \leq 350$ region
are significantly lower than that of their bulk constituents [7,8,18,36,114]. The
discrepancy between bulk densities for GeO$_2$ and MoO$_3$ and those of the as-deposited
films can be attributed to the lack heating applied to the substrate during deposition as
well as the tendency of oxygen to act as a grain refining agent, interrupting nucleation
and leading to high defect and interface volumes [13,153,216]. The low densities
calculated through XRR measurement and modeling are consistent with the amorphous
structure of the films, as evinced by the lack of crystalline character shown by the
GIXRD measurements in Figure 36. The increases in density obtained for higher values
of $U_c$ resulted from the growth of higher density, sub-stoichiometric compounds
associated with the drop in $P_{O2}$ at $350 \leq U_c$. 
Figure 36. Raw grazing incidence x-ray diffraction patterns from Mo$_x$Ge$_y$O$_z$ thin films for selected values of $U_c$. Diffraction patterns are offset for clarity.
Figure 37. Selected XRR measurements (bold) and model calculations (fine) for determination of thickness, roughness, and density.
Figure 38. Density measurements as a function of MPP capacitor bank voltage (Uc).

6.3.3 Measurement of Mo$_x$Ge$_y$O$_z$ composition and valence state

XPS survey scans, shown in Figure 39 for U$_c$ values of 300 and 380 V, were performed in order to determine the atomic concentrations of the films’ elemental constituents. The core level transitions used were O 1s, Mo 3d, Ge 2p$_{3/2}$ and C 1s. Compositions from, and binding energies of, these transitions are included in Table 14. As demonstrated in Figure 39, the concentrations of the constituent elements vary significantly for U$_c$ values of 300 and 380 V. Films deposited at U$_c$=300 V were found to contain approximately 3% C, 68% O, 4% Mo and 25% Ge, while films deposited at U$_c$=380 V had 22% C, 48% O, 15% Mo and 15% Ge. The decreased oxygen content, and the increased ratio of molybdenum to germanium, are representative of the augmentation of the molybdenum flux attributed to higher U$_c$ values.
Figure 39. XPS survey scans for Mo$_x$Ge$_y$O$_z$ films deposited for $U_c$ values of 380 V (top) and 300 V (bottom), spectra are offset for clarity. $U_c$=380 V is associated with enhanced ratios of Mo:O.

Table 14. Composition and raw binding energies of core level transitions obtained from XPS survey scans. Concentrations are not accurate to three significant figures, but they are shown to allow easier comparisons of data.

<table>
<thead>
<tr>
<th>$U_c$ (V)</th>
<th>C 1s Binding Energy (eV)</th>
<th>at. %</th>
<th>O 1s Binding Energy (eV)</th>
<th>at. %</th>
<th>Mo 3d$_{5/2}$ Binding Energy (eV)</th>
<th>at. %</th>
<th>Ge 2p$_{3/2}$ Binding Energy (eV)</th>
<th>at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>285.1</td>
<td>3.4</td>
<td>532.3</td>
<td>67.7</td>
<td>233.1</td>
<td>3.6</td>
<td>1221.1</td>
<td>25.2</td>
</tr>
<tr>
<td>310</td>
<td>284.7</td>
<td>4.0</td>
<td>532.7</td>
<td>69.2</td>
<td>232.7</td>
<td>4.6</td>
<td>1221.5</td>
<td>22.3</td>
</tr>
<tr>
<td>320</td>
<td>285.5</td>
<td>5.0</td>
<td>532.7</td>
<td>67.7</td>
<td>232.7</td>
<td>5.4</td>
<td>1221.5</td>
<td>22.0</td>
</tr>
<tr>
<td>330</td>
<td>284.9</td>
<td>7.2</td>
<td>532.9</td>
<td>67.7</td>
<td>232.9</td>
<td>6.8</td>
<td>1221.7</td>
<td>18.2</td>
</tr>
<tr>
<td>340</td>
<td>284.8</td>
<td>16.4</td>
<td>532.0</td>
<td>62.2</td>
<td>232.8</td>
<td>6.5</td>
<td>1221.6</td>
<td>14.9</td>
</tr>
<tr>
<td>350</td>
<td>285.2</td>
<td>9.5</td>
<td>532.4</td>
<td>65.4</td>
<td>232.4</td>
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<td>360</td>
<td>284.8</td>
<td>11.1</td>
<td>532.0</td>
<td>64.7</td>
<td>232.0</td>
<td>9.6</td>
<td>1221.6</td>
<td>14.6</td>
</tr>
<tr>
<td>370</td>
<td>285.2</td>
<td>13.4</td>
<td>532.4</td>
<td>61.0</td>
<td>231.6</td>
<td>10.9</td>
<td>1221.2</td>
<td>14.8</td>
</tr>
<tr>
<td>375</td>
<td>284.6</td>
<td>12.2</td>
<td>531.8</td>
<td>59.5</td>
<td>231.0</td>
<td>11.4</td>
<td>1220.6</td>
<td>16.9</td>
</tr>
<tr>
<td>380</td>
<td>285.3</td>
<td>22.4</td>
<td>531.7</td>
<td>47.5</td>
<td>229.3</td>
<td>14.8</td>
<td>1220.5</td>
<td>15.4</td>
</tr>
</tbody>
</table>
High energy resolution XPS measurements of the Ge 3d (Figure 40) and Mo 3d (Figure 41) spectra were acquired in addition to the survey spectra shown earlier in Figure 39. Measurement and analysis of high energy resolution XPS spectra was conducted in order to gain understanding of the oxidation states present within the deposited films. XPS data for the Ge 3d (Figure 40) and Mo 3d transitions (Figure 41) indicate changes in oxidation states in response to the decreased levels of $P_{O_2}$ brought on by increases in $U_c$. Beginning with the Ge 3d transition, incremental changes in $U_c$ from 300-370 V are associated with spectra centered at $BE=32.8$ eV, consistent with published values for the Ge$^{4+}$ cation associated with tetrahedral GeO$_2$ [7,220]. As $U_c$ is increased further, to 375 V, the evolution of the Ge$^{2+}$ cation, attributed to the presence of trigonal planar GeO can be observed at $BE=31.0$ eV in addition to the GeO$_2$ [7,220,221]. Note, the trigonal planar arrangement of GeO is the result of sp$^2$ hybridization between Ge and O energy levels [75,221]. Finally, conditions correlated to $U_c=380$ V led to the deposition of GeO$_2$, GeO, and elemental Ge$^0$ ($BE=29.0$ eV). Thus, chemical shifts associated with the formation of GeO$_2$, GeO, and Ge were shown to occur only at values of $U_c$ corresponding to $P_{O_2} \leq 0.05$ Pa.

High energy resolution XPS analysis of the Mo 3d transitions (Figure 41) shows quite different behavior compared to the Ge 3d transition. In contrast to the relative stability of the Ge$^{4+}$ cation shown in Figure 40, the Mo$^{6+}$ cation ($BE_{3d_{5/2}}=233.0$ eV) associated with octahedral MoO$_3$ observed for $U_c = 300-320$ V, partially reduced to Mo$^{5+}$ ($BE_{3d_{5/2}}=231.3$ eV) for a $U_c$ of 340 V, indicating the presence of the intermediate surface compound Mo$_2$O$_5$ [116-118]. The concentration of Mo$^{5+}$, relative to Mo$^{6+}$, continues to increase from 15% to 85% as $U_c$ is increased from 340 to 360 V. Formation of the Mo$^{4+}$
cation (BE$_{3d_{5/2}}$=229.2 eV) occurs at $U_c > 360$ V, indicating the presence of tetrahedral MoO$_2$ in conjunction with MoO$_3$ and Mo$_2$O$_5$. Further increases in $U_c$ lead to a larger fraction of Mo$^{4+}$ at 375 V, with partial reduction to metallic Mo$^0$ occurring at 380 V, as evidenced by the presence of the Mo 3d$_{5/2}$ component at 227.5 eV. Note that there is a variation in the binding energies of the Mo 3d doublets associated with Mo$^{6+}$ and Mo$^{5+}$. An average binding energy associated with Mo$^{6+}$ of 233.0 eV was measured for all values of $U_c$, with a maximum binding energy of 234.6 eV at $U_c=370$ V and a minimum of 232.1 eV occurring at $U_c=380$ V. Considering that all high energy resolution spectra were calibrated to the adventitious C 1s transition at 284.6 eV, these deviations from published values for various Mo-O compounds are a possible indication of the presence of Mo-O-Ge compounds, or other complex chemistries. In addition, the augmented Mo$^{6+}$ binding energies (233.0 to 234.5 eV) are similar to values (BE=233.8 eV) reported by Gil Rostra et al. attributed to a possible oxygen double bond within Mo$^{6+}$ [15].

The effects of $U_c$ on both the coordination chemistry, and the relative concentrations of the compounds present, are shown in Figure 42. Figure 42 illustrates the three main stages of reactive sputtering, namely, the (I) gettering, (II) transition, and (III) poisoned modes, indicating an excellent correlation between the onset of the transition sputtering mode and the formation of substoichiometric compounds. The Berg model was adapted, using Equations 9 and 10 to solve for the average valence states of molybdenum and germanium. Berg model predictions of the Ge and Mo valence states, as a function of $U_c$, are depicted in Figure 43. The onset of the transition regime, described using Equation 10, is identifiable based on the discernable drop in average valence number. The predicted average valence state for Mo (Figure 43a) is accurate
within zone III, but is slightly underestimated within the latter portion of the zone II.

Similar to Mo, the calculated valence state of Ge accurately predicts values within zone III, yet underestimates the average valence state at $U_c=375$. The tendency to undervalue the valence states within Figure 43 is likely a result of surface oxidation attributed to atmospheric exposure during transportation from the deposition chamber to the analysis chamber. Despite the error imparted by atmospheric exposure, the prediction of the average valence states are able to describe the general trend associated with reduction of Ge and Mo oxides as a function of increasing $U_c$.

The incremental changes in chemistry and composition brought on by systematic increases in $U_c$ are shown to produce films with gradually increasing levels of optical absorption, as demonstrated in Figure 44. As established through ligand field theory, and more recently, density functional theory, the coordination number and the arrangement of the metal-ligand bond have a significant effect on the electronic structure and subsequent optical behavior of the deposited films [117,193,194,204,221,222]. Qualitatively, films deposited from 300-320 V (Figure 44 a-c) are largely transparent with a subtle blue-gray coloration occurring at 310 V and 320 V, similar to coloration reported by Gil-Rostra et al. for mixed Mo$_x$Si$_y$O$_z$ thin films [15]. As $U_c$ is increased further, the films take on a yellow hue (Figure 44 d-g), showing slight sensitivity to the increasing proportion of the surface phase Mo$_2$O$_5$. Subsequently, at $U_c$ values from 370 V to 380 V (Figure 44 h-j), films demonstrate an evolution from dark yellow to a dark, highly absorbing appearance associated with the inclusion of MoO$_2$, Mo, and Ge in the films.
Figure 40. High energy resolution XPS measurements of the germanium 3d transition for several values of $U_c$. Note that spectra for $U_c$=310 and 330 were omitted due to similarity with $U_c$=300 and 320. Gaussian-Lorentzian lineshapes, used for peak fitting, are overlaid (thin lines) upon the raw data (bold lines). Spectra are offset for clarity.
Figure 41. High energy resolution XPS measurements of the molybdenum 3d transition for $U_c$ values from 300-380 V. Spectra are offset for clarity. Note that spectra for $U_c=310$ and 330 were omitted due to similarity with $U_c=300$ and 320. Gaussian-Lorentzian lineshapes, used for peak fitting, are overlaid (thin lines) upon the raw data (bold lines). For simplicity, only the Mo 3d$_{5/2}$ peaks are labeled.
Figure 42. Histogram depicting the relative amounts of germanium-oxygen and molybdenum oxygen compounds as a function of capacitor bank voltage ($U_c$).
Figure 43. Plot of measured and calculated average valence states for (a) Mo and (b) Ge, as determined by XPS analysis and Berg model calculations.

Figure 44. Photograph of Mo$_x$Ge$_y$O$_z$ films deposited on fused quartz substrates (a) 300 V, (b) 310 V, (c) 320 V, (d) 330 V, (e) 340 V, (f) 350 V, (g) 360 V, (h) 370 V, (i) 375 V, (j) 380 V. Note the incremental changes in coloration associated with increases in $U_c$. 
6.3.4 Optical characterization

The optical constants, n and k, and deposition rates of the MoₓGeᵧO₂ thin films were determined through measurement and fitting of iSE data after the completion of film growth. Ellipsometric modeling was employed in order to validate thicknesses reported above using XRR. Raw data acquired through iSE measurements were fit using a Cauchy dispersion relation or a general oscillator model consisting of two Lorentz oscillators. The Cauchy relation (Section 3.5, equations 12 and 13) was utilized for dielectric and semi-conducting films with a sufficient level of transparency [223,224], while the Lorentz general oscillator model (equation 16) was used in order to account for absorption features associated with the presence of elemental germanium and metallic molybdenum [225].

For the analysis of the MoₓGeᵧO₂ films as a function of Uₓ, the Cauchy relation was found to be accurate for films deposited at Uₓ ≤ 375 V. For values of Uₓ at or below 375 V, the films were shown to be composed largely of semiconducting or insulating components including Ge, GeO, GeO₂, Mo₂O₅, and MoO₃, as corroborated by the XPS results discussed earlier in section 6.3.3. At Uₓ = 380 V, the Cauchy model is no longer capable of adequately fitting the optical constants of the films, a consequence attributed to the presence of free carrier absorption related to the presence of Ge⁰, Mo⁴⁺ and Mo⁰ ions [225]. The parameters A, B, and λₒ, represent the amplitude, broadening, and centroid of the Lorentz oscillator (equation 3) [226].

\[
n(\lambda)^2 = 1 + \sum \frac{A \lambda^2}{\lambda^2 - \lambda_0^2 + iB\lambda}
\]  

(16)
Film thicknesses and the corresponding deposition rates determined from XRR and SE measurements are shown in Figure 45. The thickness deposition rate shown in Figure 45a indicates very little change as a function of $U_c$, varying between about 85 and 100 nm/min. Note that the thickness deposition rates obtained via XRR and SE agree reasonably well. Film densities obtained from XRR were used to calculate the mass deposition rates and are shown in Figure 45b. Note that densities were calculated assuming a uniform thickness over an area of 1 cm$^2$. The data in Figure 45b illustrates a non-linear increase in the mass deposition rate as a function of $U_c$. The increased densification and mass deposition rates are the direct results of a higher molybdenum sputter yield brought on by the increases in the potential applied to the cathode [83-85]. Higher applied voltages produce increased kinetic energies of the incident Ar$^+$ ions, resulting in more sputtered atoms per ion collision [83-85]. Additionally, increases in the Mo sputter yields serve to decrease the oxygen partial pressure via chemisorption on the collecting surfaces of the chamber, leading to the deposition of substoichiometric compounds and elemental components.
Figure 45. Deposition rates as calculated from XRR and SE analysis. a) Thickness deposition rates as a function of $U_c$. b) Mass deposition rates as a function of $U_c$. Deposition time for these samples was 1 minute.

The optical constants, $n$ and $k$, for the Mo$_x$Ge$_y$O$_z$ thin films are shown in Figure 46a-b, respectively. The spectral behavior of both $n$ and $k$ indicates a dependence on the value of $U_c$ used for deposition. For $U_c \leq 310$ V, $n$ is relatively flat, ranging between 1.50 and 1.40 throughout the measured spectral region (380-1700 nm). A noticeable change in the dispersion, $n(\lambda)$, occurs at $U_c=320$ V, wherein the value of $n$ begins to increase below 600 nm. Sharp increases in both $n$ and $k$ at shorter wavelengths are characteristic of the
onset of the absorption edge, correlating directly with the increased ratio of MoO$_3$ ($E_g=2.8$-3.2 eV) \cite{36,56,114} to GeO$_2$ ($E_g=5.6$-5.9) \cite{221,227,228} as determined by XPS. As evidenced by Figure 46, increases in $U_c$, from 300 to 340 V, lead to higher $n$ values, while retaining a negligible $k$. Since there is no increase in $k$ signaling the presence of absorption characteristic of substoichiometric or elemental species, the growth of $n$ is the result of the deposition of higher density components, corresponding to increases in MoO$_3$ ($n_{589}=2.2$) relative to GeO$_2$ ($n_{589}=1.6$). The correlation between density (Figure 38) and $n(\lambda)$ (Figure 46a) is in accord with the Lorentz-Lorenz relation \cite{13,210}. $U_c$ values from 340 to 375 V were associated with further increases in both $n$ and $k$, indicating that the optical properties of the Mo$_x$Ge$_y$O$_z$ films are significantly affected by small, incremental changes in $U_c$. 

Figure 46. Plot of the refractive index (a) and extinction coefficient (b) as a function of wavelength for the different capacitor bank voltages ($U_c$).
Optical gap measurements were performed to determine the onset of interband absorption features correlated to the presence of different chemical species within the films. Due to the lack of long range crystalline order, as well as the large variety of valence states present within the Mo\textsubscript{x}Ge\textsubscript{y}O\textsubscript{z} films, it would be difficult to fully parameterize the effect that each has upon the electronic structure of the films. However, the combination of XRR, XPS, SE, and UV-VIS-NIR spectrophotometry provides an adequate correlation between the optical and chemical properties of the films. The calculation of the optical gap was performed using Tauc’s plots, as shown in Figure 47. In the present case, the Tauc’s plots were created using the optical absorption coefficient, $\alpha$, calculated using the following equations:

$$\alpha = -\frac{1}{d} \ln \left( \frac{T}{1-R^2} \right)$$  \hspace{1cm} (17)

$$\alpha \nu = (\nu - E_g) \eta$$  \hspace{1cm} (18)

Note that T and R represent transmittance and reflectance, respectively, while $d$ accounts for the thickness of the film (Equation 17). Equation 18 describes the relationship between $\alpha$, photon energy ($\nu$), and $(E_g)$ [44,80,210]. The exponent, $\eta$, is equal to 2, as is the convention with amorphous semiconductors [29,44,151,229]. As reported by Tauc et al., a lack of long range crystalline order prohibits the occurrence of an indirect transition due to the non-conservation of wave vectors [229,230].

The chemical constituents identified by XPS include GeO\textsubscript{2}, GeO, Ge, MoO\textsubscript{3}, Mo\textsubscript{2}O\textsubscript{5}, MoO\textsubscript{2}, and Mo. These compounds and elements have different electronic structures, namely, wide optical gap semiconductors in the case of GeO\textsubscript{2}, GeO [7,8,221] and MoO\textsubscript{3} [36,37,44,231], semiconducting Ge, and electrically conductive materials such
as Mo and MoO$_2$ [117,120,222,232,233]. Published values for the band energies of each of the chemical constituents present are listed in Table 15.

Table 15. List of published optical gaps for selected oxides of germanium and molybdenum.

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Compound</th>
<th>$E_g$ (eV)</th>
<th>Reference no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge 0</td>
<td>Ge</td>
<td>0.67-0.88</td>
<td>[7,8,221]</td>
</tr>
<tr>
<td>2+</td>
<td>GeO*</td>
<td>2.8-4.0</td>
<td>[221,234]</td>
</tr>
<tr>
<td>4+</td>
<td>GeO$_2$</td>
<td>5.9-6.1</td>
<td>[7,8,221,228]</td>
</tr>
<tr>
<td>Mo 0</td>
<td>Mo</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>4+</td>
<td>MoO$_2$</td>
<td>0</td>
<td>[117,120,232,233]</td>
</tr>
<tr>
<td>5+</td>
<td>Mo$_2$O$_5$**</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>6+</td>
<td>MoO$_3$</td>
<td>2.7-3.2</td>
<td>[36,56,133,235]</td>
</tr>
</tbody>
</table>

*values are from numerical simulations

**Note that Mo$_2$O$_5$ is classified as a “surface phase” with no known bulk structure [116-118]

Figure 47. Tauc's plot for $E_g$ calculations assuming a Tauc’s gap commonly associated with amorphous materials, for films deposited at $U_c$ ranging from 300 to 380 V. Dotted lines are representative of least squares fitting to extrapolate the linear portion of $a h v^{1/2}$ to $h v=0$ eV.
The Tauc’s plots shown in Figure 47 are indicative of large changes in the respective values of $\alpha$ as a function of $U_c$. Note the stepwise behavior of the curves within the Tauc plot (Figure 47). The additional absorption features in Figure 47 occur at energies below the onset of the absorption edge, and are consistent with multi-phonon interaction associated with indirect band-to-band transitions. Values of $(\alpha \nu)^{1/2}$ are shown to gradually increase with $U_c$ from 320 to 360 V. As shown in Figure 47, there appears to be little change in $\alpha$ for $U_c$ from 300 to 320 V, while a further increase of $\alpha$ can be seen for $U_c=340$ and 360. Finally, increases of $U_c$, from 360 to 380 V, were shown to correspond to a large increase in $\alpha$ over the measured spectral region. In order to quantitatively determine $E_g$, the linear regions within Figure 47 were fit using linear regression, allowing for the calculation of $E_g$ by the determination of the x-intercept, as described in Equation 5. All linear fits used for the $E_g$ calculation had $R^2$ values above 0.99, indicating excellent fits. Figure 48 illustrates the relationship between $E_g$ and $P_{O_2}$ with $U_c$ for the Mo$_x$Ge$_y$O$_z$ films. As shown in Figure 48, $E_g$ values decrease almost linearly within the poisoned regime (III), from 3.4 (±0.2) eV for a $U_c$ of 300, to 3.0 (±0.1) eV at $U_c$=330 V. This approximate linear decrease of $E_g$ within the poisoned regime (III) is directly related to the increased ratio of Mo$^{6+}$ MoO$_3$ ($E_g$=3.2-2.8) to Ge$^{4+}$ GeO$_2$ ($E_g$=5.9-6.1), as determined by XPS analysis.

Note that $E_g$ values shown in Figure 48 are significantly lower than values for bulk germanium ($5.9 \leq E_g \leq 6.0$) [7,8,221,228]; this is a potential result of the formation of Mo-O-Ge bonds. Similar complex bonding structures, involving oxygen sharing between octahedral metal oxides and tetrahedral oxides of both SiO$_2$ [15] and GeO$_2$ [236] have been reported for reactively sputtered mixed oxide compounds. Upon entering the
transition regime (II), $E_g$ remains relatively constant for $U_c$ values of 340, 350 and 360 V, corresponding to values of 3.0 (±0.2), 3.0 (±0.2), and 2.9 (±0.1) eV, respectively. The minimal change observed in $E_g$ from 340 to 360 V indicates that $E_g$ is largely unaffected by the presence of the surface phase Mo$_2$O$_5$ (Mo$^{5+}$). Further increases in $U_c$, from 370 to 375 V are characterized by a significant decrease in $E_g$, from 2.4 (±0.2) to 1.8 (±0.2) eV. This marked decrease in $E_g$ 370 and 375 V is directly related to the presence of MoO$_2$ (Mo$^{4+}$) and, concurrently, GeO (Ge$^{2+}$). The lowest value of $E_g$, 0.4 (±0.1) eV, was found to occur at $U_c$=380 V, a result that is in line with the presence of 4% Mo and 30% MoO$_2$. Note that XPS also detected the presence of nearly 6% Ge, as shown in Figure 42.

Investigation of the relationship between $E_g$ and $U_c$ has indicated that increases in $U_c$ can be correlated to decreases in the magnitude of $E_g$, the behavior of which is intimately coupled with $P_{O_2}$, as illustrated in Figure 48. A detailed physical explanation of the changes in $E_g$, as a function of the processing parameter $U_c$, is presented and discussed in the next section.
Figure 48. Calculated values of $E_g$ for $U_c$ from 300 to 380 V. The vertical dotted lines are included to signify the onset of the (III) poisoned, (II) transition, and (I) gettering modes associated with reactive sputtering.

Table 16. Film thicknesses used for the calculation of $E_g$. Thicknesses were measured using spectroscopic ellipsometry.

<table>
<thead>
<tr>
<th>$U_c$ (V)</th>
<th>Thickness (nm)</th>
<th>$E_g$ (eV)</th>
<th>Error (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>276</td>
<td>3.4</td>
<td>0.2</td>
</tr>
<tr>
<td>310</td>
<td>279</td>
<td>3.2</td>
<td>0.2</td>
</tr>
<tr>
<td>320</td>
<td>276</td>
<td>3.1</td>
<td>0.2</td>
</tr>
<tr>
<td>330</td>
<td>288</td>
<td>3.0</td>
<td>0.1</td>
</tr>
<tr>
<td>340</td>
<td>294</td>
<td>3.0</td>
<td>0.2</td>
</tr>
<tr>
<td>350</td>
<td>291</td>
<td>3.0</td>
<td>0.2</td>
</tr>
<tr>
<td>360</td>
<td>285</td>
<td>2.9</td>
<td>0.1</td>
</tr>
<tr>
<td>370</td>
<td>285</td>
<td>2.4</td>
<td>0.2</td>
</tr>
<tr>
<td>375</td>
<td>288</td>
<td>1.8</td>
<td>0.2</td>
</tr>
<tr>
<td>380</td>
<td>261</td>
<td>0.4</td>
<td>0.1</td>
</tr>
</tbody>
</table>
6.3.5 Process-optical property correlation

Studies of the optical behavior, focusing on n, k, and E_g, have indicated incremental changes associated with decreases in P_O2 as a result of increasing U_c. The films’ coloration can be directly attributed to the magnitude of E_g, as no other dominant absorption features are shown within visible wavelengths, as depicted in Figure 46b. One trend that is particularly noteworthy is the correlation between film chemistry and E_g. Based on the complex chemistry and the amorphous structure of the films, it is difficult to quantitatively parameterize the effect of each coordination compound on the resulting band structure. However, through the use of principles set forth by ligand field theory, a comprehensive, albeit qualitative, explanation of the decrease in E_g with increasing U_c can be reached. As depicted in Figure 42 and Figure 48, it is evident that each large change in E_g can be associated with a change in coordination chemistry, with the exception of films deposited within the poisoned regime (III) where the properties can be correlated to the existence of fully stoichiometric MoO_3 and GeO_2. The transparent films deposited at a U_c of 300 V are a direct result of the large E_g values associated with Mo^{6+} and Ge^{4+} coordination compounds. The large E_g of MoO_3 is the result of the splitting of 4d orbitals attributed to the static electric field between the 6 O^{2-} anions surrounding the central Mo^{6+} cation, leading to a MoO_6 octahedral base unit [29]. The resulting metal-ligand bonding between Mo and O leads to the splitting of the Mo 4d levels into anti-bonding t_{2g} and bonding e_g sets. These anti-bonding t_{2g} sets are unfilled in MoO_3, resulting in an energy gap of 2.7-3.2 eV between the Mo 4d (t_{2g}) and O 2p (p_π) levels [29,116,237]. Note that GeO_2, based on the tetrahedral GeO_4 structural unit, has an E_g of 5.9-6.1 eV, thus rendering it incapable of absorbing visible wavelengths. As U_c is
increased further, to 310 and 320 V, a slight blue-gray tint is observed, corresponding to $E_g$ values of 3.2 ($\pm 0.2$) and 3.1 ($\pm 0.2$) eV. Previous studies have observed blue coloration in slightly reduced MoO$_3$ films with oxygen vacancies, denoted as MoO$_{3-x}$ [15,116,237]. The mechanism attributed to the blue coloration of MoO$_{3-x}$ has been related to the onset of free carrier absorption as a result of electrons being excited to the previously unfilled t$_{2g}$ band [29,116,237]. Increasing $U_c$ to 330 V corresponds to films with an $E_g$ of 3.0 ($\pm 0.2$) eV, leading to a yellow tint associated with the increased Mo:Ge ratio. An $E_g$ of 3.0 ($\pm 0.2$) eV is consistent with reported optical gaps for MoO$_3$ [36,37], and is related to absorption of blue light ($\lambda < 440$ eV), leading to a yellow coloration [204,238]. The yellow hue of the films persists, becoming more intense within the transition regime (II) for $U_c$ values of 340 to 360, and is correlated to a 33% increase in the amount of Mo$_2$O$_5$ (Figure 42). As the amount of Mo$_2$O$_5$ increases from 340 to 360 V, the slope of $a h \nu^{1/2}$ ($h\nu$) also becomes larger. Increases in the slope of $a h \nu^{1/2}$ ($h\nu$) (Figure 47) can be attributed to the augmentation of electron-electron and impurity scattering events related to increased doping levels in indirect semiconductors [80]. The slope, and magnitude of $a h \nu^{1/2}$ ($h\nu$) continue to rise alongside $U_c$ related to increases in Mo$^{x<6+}$ and Ge$^{x<4+}$ cation concentration. Further decreases in $E_g$ occur for $U_c$ settings of 370 and 375 V, as a result of reaching $P_{O2}$ values conducive to the formation of MoO$_2$. MoO$_2$ is reported to have metal-like conductivity as a result of Mo-Mo bond formation [117]. Note that GeO is also present within films deposited where $U_c \geq 370$ V, and GeO has been reported to have calculated $E_g$ values ranging from 2.8-4.0 eV [221,234], potentially bolstering the yellow appearance associated with $E_g$ values near 3.0 ($\pm 0.2$) eV. Finally, the film deposited at
U_c=380 V has minimal optical transparency as a result of the presence of elemental Mo and Ge.

6.4 Summary and conclusions

Based upon the results presented within this study, it is evident that the optical absorption, and correspondingly, the coloration of amorphous Mo_xGe_yO_z thin films can be systematically varied by modifying the MPPMS capacitor bank voltage, U_c. Increases in U_c have been shown to decrease P_O2 due to the oxygen chemisorption from the high fraction of Mo within the MPPMS deposition flux. As shown from the XPS measurements and peak fitting, decreases in P_O2 are directly related to increases in the ratio of Mo to Ge within the deposition flux and film densification associated with the presence of substoichiometric compounds including GeO (Ge^{2+}), Mo_2O_5 (Mo^{5+}), and MoO_2 (Mo^{4+}). Furthermore, the presence, and relative amounts, of the different coordination complexes can be directly correlated to decreases in both P_O2 and E_g. The process-property relationship between U_c and E_g, established within this work, allows for the deposition of Mo_xGe_yO_z films with E_g values that are able to be tailored between 3.4 and 0.4 eV. In addition, analysis of the optical constants obtained from spectroscopic ellipsometry also indicated incremental increases in both n and k, as a function of increasing U_c. The high degree of control available for both n and k shows promise in the design and fabrication of multilayer interference coatings that require precise control over the optical constants. The hybrid DCMS-MPPMS co-deposition method used in this work has been shown to be an effective and highly controllable method for depositing mixed-valent ionic glass coatings with absorption features spanning the breadth of the visible spectrum.
7. SUMMARY AND CONCLUSIONS

7.1 Germanium oxide

Germanium oxide (GeO\textsubscript{x}) films were grown on (100) Si substrates by reactive DC magnetron sputter-deposition using a Ge target. The effects of oxygen gas fraction, \( \Gamma \), on the deposition rate, structure, chemical composition, and optical properties of GeO\textsubscript{x} films have been investigated. The chemistry of the films exhibits an evolution from pure Ge to a Ge+GeO+GeO\textsubscript{2} mixed phase and then finally to GeO\textsubscript{2} upon increasing \( \Gamma \) from 0.00 to 1.00. GIXRD analysis indicates that the GeO\textsubscript{x} films were amorphous. The optical properties probed by spectroscopic ellipsometry indicate that the effect of \( \Gamma \) is significant on the optical constants of GeO\textsubscript{x} films. The measured index of refraction (n) at a wavelength (\( \lambda \)) of 550 nm is 4.67 for films grown without any oxygen, indicating behavior characteristic of semiconducting Ge. The transition from germanium to mixed Ge+GeO+GeO\textsubscript{2} composition is associated with a characteristic decrease in n (\( \lambda=550 \) nm) to 2.62 and occurs at \( \Gamma=0.25 \). Finally n drops to 1.60 for \( \Gamma=0.50-1.00 \), where the films become GeO\textsubscript{2}.

Work exploring the Ge-O binary system yielded a correlation between the O\textsubscript{2} gas fraction (\( \Gamma \)), chemical composition (Ge chemical state) and optical properties (n and k) of DC sputtered GeO\textsubscript{x}. Such a correlation should be useful to select the processing conditions in order to tune the chemical composition, and hence, the optical constants of
GeO\textsubscript{x} films. Establishment of the dielectric-semiconductor transition of thin Germanium films is especially valuable within the optical coatings and telecommunications industries, where the deposition of highly dense GeO\textsubscript{2} thin films, with precise optical performance is required.

7.2 Molybdenum oxide

Molybdenum oxide films were deposited using MPPMS from a molybdenum target in a reactive environment where the flow rate of oxygen was varied from 0 – 2.00 sccm. By varying the amount of reactive oxygen available during deposition, the composition of the films ranged from metallic Mo to fully stoichiometric MoO\textsubscript{3} when the molybdenum target became poisoned, due to the formation of a dielectric surface oxide coating. Film compositions were verified using high energy resolution XPS. Target poisoning occurred at an oxygen flow rate of 1.25 sccm and reversed when the flow rate decreased to about 1.00 sccm. MoO\textsubscript{3} films deposited via MPPMS had densities of 3.8 g cm\textsuperscript{-3}, 81% of the density of crystalline \(\alpha\)-MoO\textsubscript{3} as determined by XRR. In addition, XRR and AFM data showed sub-nanometer surface roughness values. From spectroscopic ellipsometry the measured refractive index of the MoO\textsubscript{3} films at 589 nm was 1.97 with extinction coefficient values less than 0.02 at wavelengths above the measured absorption edge of 506 nm (2.45 eV).

Exploration of the Mo-O system, deposited using MPPMS, was of particular interest due to the fact that no studies using the MPPMS for the deposition of MoO\textsubscript{3} exist at this time. Based on measurement of density, absorption, and chemical state, it can be concluded that films deposited at oxygen flow rates at and below \(Q_{O_2}=0.75\) sccm were
metallic, while films deposited at and above $Q_{O_2}=1.00$ sccm were shown to be insulating. The identification of the metal-insulator transition provides a useful process-property relationship for increased understanding of the processing requirements needed to deposit highly dense, transparent MoO$_3$ thin films with average surface roughness values below 1 nm. This work establishes the proper experimental conditions required to deposit high quality MoO$_x$ thin films with optical properties similar to those of bulk Mo and MoO$_3$.

7.3 Rhenium oxide

Mixed-valent rhenium oxide thin films were deposited using reactive magnetron sputtering employing a metallic rhenium target within an oxygen-argon environment. The oxygen and argon flow rates were systematically varied, while the extinction coefficient, $k$, of the deposited layers was monitored using \textit{in situ} spectroscopic ellipsometry. \textit{In situ} monitoring was used to identify absorption features specific to ReO$_3$, namely, the minimization of $k$ brought on by the gap between interband absorption features in the UV at 310 nm and the onset of free electron absorption at wavelengths above 540 nm. Based on these results, oxygen flow ratios of 50 and 60 percent were shown to have optical properties characteristic of ReO$_3$, and thus, were selected for detailed \textit{ex situ} characterization. Chemical analysis via XPS confirmed that all films were mixed-valent, consisting largely of ReO$_3$, with small contributions from Re$_2$O$_3$, ReO$_2$ and Re$_2$O$_7$. Additional monitoring of the chemistry, as a function of environmental exposure time, indicated a correlation between structural instability and the presence of Re$_2$O$_3$ and Re$_2$O$_7$.  

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Despite having only a 10% percent difference in their respective oxygen flow ratios, rhenium oxide films deposited at $\Gamma=0.5$ and 0.6 have disparate optical and chemical properties, especially as a function of environmental exposure time. While both the Re$^{7+}$ and Re$^{3+}$ oxidations states were prone to moisture based degradation, each were shown to degrade as a result of different chemical processes. While the Re$^{7+}$ state was shown to slowly degrade due to the formation of HReO$_4$, the Re$^{3+}$ state rapidly decomposed into metallic Re$^0$ and hydrated ReO$_2$ as a result of catalytic disproportionation. Despite the degradation mechanisms associated with exposure to moisture, films deposited at an oxygen level sufficient to preclude the formation of Re$^{3+}$ were able to retain their optical and chemical properties throughout the 30 day exposure period. Increasing the stability of mixed-valent Re-O films could give rise to more widespread use of rhenium in optics and catalysis, especially in applications where mild moisture exposure is unavoidable.

7.4 Mixed-valent oxides of molybdenum and germanium (Mo$_x$Ge$_y$O$_z$)

Mixed-valent oxides of molybdenum and germanium were deposited simultaneously using reactive magnetron co-deposition within an oxygen-argon environment. The films’ stoichiometry, optical and physical properties were varied through changes in oxygen partial pressure induced by systematic variation of the potential applied to the molybdenum cathode. The oxygen partial pressure was determined from the drop in pressure as measured by a capacitance manometer, assuming constant argon partial pressure. To facilitate deposition, a constant power of 100 W DC was applied to the germanium cathode, while power was applied to the molybdenum target using a modulated pulse power supply. Modulated pulse power magnetron
sputtering was used due to its ability to generate high target power densities, allowing for rapid reduction of oxygen on the surface of the “oxygen poisoned” molybdenum cathode, as well as for its highly metallic plasma resulting in increased oxygen-gettering capability. Changes in the modulated pulse power supply’s capacitor bank voltage, stepped from settings of 300 to 380 V, resulted in films ranging from mixtures of transparent GeO₂ (Ge⁴⁺) and MoO₃ (Mo⁶⁺) to the introduction of various absorptive ionic species including Mo⁵⁺, Mo⁴⁺, Ge²⁺ and Ge⁰, as determined from x-ray photoelectron spectroscopy. The presence of each of the aforementioned ions results in characteristic changes in the films’ band energies and optical absorption, measured using UV-VIS-NIR optical spectrophotometry. MoₓGeᵧO₂ thin films grown using this method have been shown to have optical gaps that are able to be tailored between 3.4 eV and 0.4 eV, spanning useful ranges for devices operating in the visible and near-infrared.

Considering the data presented within this work, it is apparent that the optical properties and the resulting absorption of amorphous MoₓGeᵧO₂ thin films can be precisely varied as a function of the MPPMS capacitor bank voltage, Uₐ. The augmentation of Uₐ has been shown to incrementally lower P₀₂ via oxygen chemisorption attributed to the high fraction of Mo within the deposition flux. In addition, this project devised a variant of the Berg model capable of predicting the average valence state of the deposited Mo and Ge oxides within a reasonable degree of accuracy. Understanding of the correlation between the predicted chemistry and optical properties allows for the user to deposit thin films with the desired level of optical absorption. As a result of the combination of empirical investigation and modeling, the high level of control over n and k shows promise for the design and fabrication of multilayer interference filters that
requiring precise optical constants. The hybrid DCMS-MPPMS co-deposition method developed within this work has been shown to be an effective and scalable method for depositing mixed-valent ionic glass coatings with absorption features spanning the breadth of the visible spectrum.
8. FUTURE WORK

Future work will employ the use of the hybrid MPPMS-DCMS co-deposition technique on different materials systems employing combinations of transition metals. Specifically, work on the WO$_3$-TiO$_x$ material system has shown promise for transparent conductivity and free electron absorption of near-infrared wavelengths [29,210]. In addition, heat treatment of mixed oxide samples could give rise to the presence of nanocrystalline features with interesting structural, optical, and electronic properties. The combined deposition and modeling techniques established within this work provide the tools to deposit multiple component thin films with a large variety of optical properties within a given material system. Currently, one of the largest challenges is to identify the proper constituent materials. Use of the methods described in this dissertation, in conjunction with first-principles modeling of the optical response of selected transition metal oxide systems, could be used to fabricate thin films with engineered absorption features over specified wavelength ranges.
9. PUBLICATIONS

The results of the research described within this dissertation can be found within the following publications:


N.R. Murphy, L. Sun, J.G Jones, J.T. Grant “Co-deposition of Mixed-valent Oxides of Molybdenum and Germanium (Mo\textsubscript{x}Ge\textsubscript{y}O\textsubscript{z}): A Route to Tailored Optical Absorption” Submitted to Thin Solid Films.
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APPENDIX A

TWO TARGET REACTIVE SPUTTERING MODEL GUI
APPENDIX B

CORRECTION OF MPPMS VOLTAGE AND CURRENT FOR SPUTTER YIELD CALCULATION

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<thead>
<tr>
<th>$U_c$ (V)</th>
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<td>330</td>
<td>215</td>
<td>0.44</td>
<td>94.6</td>
</tr>
<tr>
<td>340</td>
<td>232</td>
<td>0.51</td>
<td>119.0</td>
</tr>
<tr>
<td>350</td>
<td>255</td>
<td>0.72</td>
<td>184.2</td>
</tr>
<tr>
<td>360</td>
<td>275</td>
<td>0.87</td>
<td>239.6</td>
</tr>
<tr>
<td>370</td>
<td>302</td>
<td>1.20</td>
<td>363.4</td>
</tr>
<tr>
<td>375</td>
<td>323</td>
<td>1.47</td>
<td>474.2</td>
</tr>
<tr>
<td>380</td>
<td>372</td>
<td>2.67</td>
<td>991.9</td>
</tr>
</tbody>
</table>

MPPMS voltages and currents were corrected in order to account for the inability to discharge completely throughout the poisoned regime, where both the anode and the cathode are coated with a thin layer of dielectric material. The observed discharge behavior is shown within Figure 35. Corrected values were obtained by calculating the average voltages and currents throughout the 1 ms pulse, and subtracting the average value of the voltage and current magnitude for the 0.9 ms following the pulse.
APPENDIX C

TWO TARGET REACTIVE SPUTTERING MODEL MATLAB CODE

function varargout = x20150114_BERGmodel_2Target_GUI(varargin)
% X20150114_BERGMODEL_2TARGET_GUI MATLAB code for
% X20150114_BERGmodel_2Target_GUI.fig
% X20150114_BERGMODEL_2TARGET_GUI, by itself, creates x5 new
% X20150114_BERGMODEL_2TARGET_GUI or raises the existing
% singleton*.
% H = X20150114_BERGMODEL_2TARGET_GUI returns the handle to x5 new
% X20150114_BERGMODEL_2TARGET_GUI or the handle to
% the existing singleton*.
%
% X20150114_BERGMODEL_2TARGET_GUI('CALLBACK',hObject,eventData,handles,..)
% calls the local
% function named CALLBACK in X20150114_BERGMODEL_2TARGET_GUI.x8
% with the given input arguments.
% X20150114_BERGMODEL_2TARGET_GUI('Property','Value',...) creates
% x5 new X20150114_BERGMODEL_2TARGET_GUI or raises the
% existing singleton*. Starting from the left, property value
% pairs are
% applied to the GUI before
% X20150114_BERGmodel_2Target_GUI_OpeningFcn gets called. An
% unrecognized property name or invalid value makes property
% application
% stop. All inputs are passed to
% X20150114_BERGmodel_2Target_GUI_OpeningFcn via varargin.
% *See GUI Options on GUIDE's Tools menu. Choose "GUI allows only
% one
% instance to run (singleton)".
% See also: GUIDE, GUIDATA, GUIDATA

% Edit the above text to modify the response to help
% x20150114_BERGmodel_2Target_GUI

% Last Modified by GUIDE v2.5 14-Jan-2015 20:00:30

% Begin initialization code - DO NOT EDIT
gui_Singleton = 1;
gui_State = struct('gui_Name', mfilename, ...
    'gui_Singleton', gui_Singleton, ...
function x20150114_BERGmodel_2Target_GUI_OpeningFcn(hObject, eventdata, handles, varargin)
% This function has no output args, see OutputFcn.
% hObject    handle to figure
% eventdata  reserved - to be defined in x5 future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)
% varargin   command line arguments to x20150114_BERGmodel_2Target_GUI
% (see VARARGIN)

% Choose default command line output for
x20150114_BERGmodel_2Target_GUI
handles.output = hObject;

% Update handles structure
guidata(hObject, handles);

% UIWAIT makes x20150114_BERGmodel_2Target_GUI wait for user response
% (see UIRESUME)
% uiwait(handles.figure1);

function varargout = x20150114_BERGmodel_2Target_GUI_OutputFcn(hObject, eventdata, handles)
% varargout  cell array for returning output args (see VARARGOUT);
% hObject    handle to figure
% eventdata  reserved - to be defined in x5 future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Get default command line output from handles structure
varargout{1} = handles.output;

% --- Executes just before x20150114_BERGmodel_2Target_GUI is made visible.
function x20150114_BERGmodel_2Target_GUI_OpeningFcn(hObject, eventdata, handles, varargin)
% hObject    handle to figure
% eventdata  reserved - to be defined in x5 future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)
% varargin   command line arguments to x20150114_BERGmodel_2Target_GUI
% (see VARARGIN)

% Choose default command line output for
x20150114_BERGmodel_2Target_GUI
handles.output = hObject;

% Update handles structure
guidata(hObject, handles);

% UIWAIT makes x20150114_BERGmodel_2Target_GUI wait for user response
% (see UIRESUME)
% uiwait(handles.figure1);

% --- Outputs from this function are returned to the command line.
function varargout = x20150114_BERGmodel_2Target_GUI_OutputFcn(hObject, eventdata, handles)
% varargout  cell array for returning output args (see VARARGOUT);
% hObject    handle to figure
% eventdata  reserved - to be defined in x5 future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Get default command line output from handles structure
varargout{1} = handles.output;

% --- Executes just before x20150114_BERGmodel_2Target_GUI is made
% visible.
function x20150114_BERGmodel_2Target_GUI_OpeningFcn(hObject, eventdata, handles, varargin)
% hObject    handle to figure
% eventdata  reserved - to be defined in x5 future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)
% varargin   command line arguments to x20150114_BERGmodel_2Target_GUI
% (see VARARGIN)

% Choose default command line output for
x20150114_BERGmodel_2Target_GUI
handles.output = hObject;

% Update handles structure
guidata(hObject, handles);

% UIWAIT makes x20150114_BERGmodel_2Target_GUI wait for user response
% (see UIRESUME)
% uiwait(handles.figure1);

% --- Outputs from this function are returned to the command line.
function varargout = x20150114_BERGmodel_2Target_GUI_OutputFcn(hObject, eventdata, handles)
% varargout  cell array for returning output args (see VARARGOUT);
% hObject    handle to figure
% eventdata  reserved - to be defined in x5 future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Get default command line output from handles structure
varargout{1} = handles.output;
function Yc_Callback(hObject, eventdata, handles)
% hObject    handle to Yc (see GCBO)
% eventdata  reserved - to be defined in x5 future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'String') returns contents of Yc as text
% str2double(get(hObject,'String')) returns contents of Yc as x5
double

% --- Executes during object creation, after setting all properties.
function Yc_CreateFcn(hObject, eventdata, handles)
% hObject    handle to Yc (see GCBO)
% eventdata  reserved - to be defined in x5 future version of MATLAB
% handles    empty - handles not created until after all CreateFcns
% called

% Hint: edit controls usually have x5 white background on Windows.
% See ISPC and COMPUTER.
if ispc && isequal(get(hObject,'BackgroundColor'),
    get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor','white');
end

function Ym_Callback(hObject, eventdata, handles)
% hObject    handle to Ym (see GCBO)
% eventdata  reserved - to be defined in x5 future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'String') returns contents of Ym as text
% str2double(get(hObject,'String')) returns contents of Ym as x5
double

% --- Executes during object creation, after setting all properties.
function Ym_CreateFcn(hObject, eventdata, handles)
% hObject    handle to Ym (see GCBO)
% eventdata  reserved - to be defined in x5 future version of MATLAB
% handles    empty - handles not created until after all CreateFcns
% called

% Hint: edit controls usually have x5 white background on Windows.
% See ISPC and COMPUTER.
if ispc && isequal(get(hObject,'BackgroundColor'),
    get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor','white');
end

function At_Callback(hObject, eventdata, handles)
% hObject    handle to At (see GCBO)

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function At_CreateFcn(hObject, eventdata, handles)

function Ac_CreateFcn(hObject, eventdata, handles)

function a_Callback(hObject, eventdata, handles)

function Ac_Callback(hObject, eventdata, handles)

function a_Callback(hObject, eventdata, handles)
% Hints: get(hObject,'String') returns contents of a as text
% str2double(get(hObject,'String')) returns contents of a as double

% --- Executes during object creation, after setting all properties.
function a_CreateFcn(hObject, eventdata, handles)
% hObject    handle to a (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns
called

% Hint: edit controls usually have white background on Windows.
% See ISPC and COMPUTER.
if ispc && isequal(get(hObject,'BackgroundColor'),
                   get(0,'defaultUicontrolBackgroundColor'))
  set(hObject,'BackgroundColor','white');
end

function I_Callback(hObject, eventdata, handles)
% hObject    handle to I (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'String') returns contents of I as text
% str2double(get(hObject,'String')) returns contents of I as double

% --- Executes during object creation, after setting all properties.
function I_CreateFcn(hObject, eventdata, handles)
% hObject    handle to I (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns
called

% Hint: edit controls usually have white background on Windows.
% See ISPC and COMPUTER.
if ispc && isequal(get(hObject,'BackgroundColor'),
                   get(0,'defaultUicontrolBackgroundColor'))
  set(hObject,'BackgroundColor','white');
end

function S1_Callback(hObject, eventdata, handles)
% hObject    handle to S1 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'String') returns contents of S1 as text
% str2double(get(hObject,'String')) returns contents of S1 as double

% --- Executes during object creation, after setting all properties.
function S1_CreateFcn(hObject, eventdata, handles)
% hObject    handle to S1 (see GCBO)
% eventdata  reserved - to be defined in future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: edit controls usually have white background on Windows.
%       See ISPC and COMPUTER.
if ispc && isequal(get(hObject,'BackgroundColor'),
get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor','white');
end

function T_Callback(hObject, eventdata, handles)
% hObject    handle to T (see GCBO)
% eventdata  reserved - to be defined in future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'String') returns contents of T as text
%        str2double(get(hObject,'String')) returns contents of T as double

% --- Executes during object creation, after setting all properties.
function T_CreateFcn(hObject, eventdata, handles)
% hObject    handle to T (see GCBO)
% eventdata  reserved - to be defined in future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hint: edit controls usually have white background on Windows.
%       See ISPC and COMPUTER.
if ispc && isequal(get(hObject,'BackgroundColor'),
get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor','white');
end

function M_Callback(hObject, eventdata, handles)
% hObject    handle to M (see GCBO)
% eventdata  reserved - to be defined in future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'String') returns contents of M as text
%        str2double(get(hObject,'String')) returns contents of M as double
% --- Executes during object creation, after setting all properties.
function M_CreateFcn(hObject, eventdata, handles)
% hObject    handle to M (see GCBO)
% eventdata  reserved - to be defined in x5 future version of MATLAB
% handles    empty - handles not created until after all CreateFcns
called

% Hint: edit controls usually have x5 white background on Windows.
% See ISPC and COMPUTER.
if ispc & isequal(get(hObject,'BackgroundColor'),
get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor','white');
end

function O_Callback(hObject, eventdata, handles)
% hObject    handle to O (see GCBO)
% eventdata  reserved - to be defined in x5 future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'String') returns contents of O as text
%        str2double(get(hObject,'String')) returns contents of O as x5
double

% --- Executes during object creation, after setting all properties.
function O_CreateFcn(hObject, eventdata, handles)
% hObject    handle to O (see GCBO)
% eventdata  reserved - to be defined in x5 future version of MATLAB
% handles    empty - handles not created until after all CreateFcns
called

% Hint: edit controls usually have x5 white background on Windows.
% See ISPC and COMPUTER.
if ispc & isequal(get(hObject,'BackgroundColor'),
get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor','white');
end

% --- Executes on button press in pushbutton1.
function pushbutton1_Callback(hObject, eventdata, handles)
% hObject    handle to pushbutton1 (see GCBO)
% eventdata  reserved - to be defined in x5 future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)
guida(hobject,handles);

% Flow conditions-------------------------------------
P1=0.00001:0.005:5; %reactive gas partial pressure mTorr
P=P1*0.133; %reactive gas pressure Pa
S1=str2double(get(handles.S1,'String'));
S=S1/1000; %m^3/s
%1sccm=7.4*10^-7 moles/second
%1mol=22.4 liters

%Target 1 conditions-----------------------------
Yc1=str2double(get(handles.Yc,'String')); %compound sputter yield
Ym1=str2double(get(handles.Ym,'String')); %Target sputter yield
Yo1=str2double(get(handles.Yo1,'String')); %Oxygen sputter yield
At1=str2double(get(handles.At,'String')); %Target Area (m^2)
a1=str2double(get(handles.a,'String')); %sticking coeff
I1=str2double(get(handles.I,'String')); %current (C/s)
M1=str2double(get(handles.M,'String')); %Metal
O1=str2double(get(handles.O,'String')); %Oxygen
J1=(I1/At1); %electron flux C/m^2*s
Yo1=str2double(get(handles.Yo1,'String')); %excess oxygen sputter yield

%Target 2 conditions-----------------------------
Yc2=str2double(get(handles.Yc2,'String')); %compound sputter yield
Ym2=str2double(get(handles.Ym2,'String')); %Target sputter yield
Yo2=str2double(get(handles.Yo2,'String')); %Oxygen sputter yield
At2=str2double(get(handles.At2,'String')); %Target Area (m^2)
a2=str2double(get(handles.a2,'String')); %sticking coeff
I2=str2double(get(handles.I2,'String')); %current (C/s)
M2=str2double(get(handles.M2,'String')); %Metal
O2=str2double(get(handles.O2,'String')); %Oxygen
J2=(I2/At2); %electron flux C/m^2*s
Yo2=str2double(get(handles.Yo2,'String')); %excess oxygen sputter yield

T=str2double(get(handles.T,'String')); %Temperature
RGmass=str2double(get(handles.RG,'String')); %Mass
Ac=str2double(get(handles.Ac,'String')); %collector (substrate area) (m^2)

t1c1=1; %mass target atom target 1
t1c2=1; %mass reactive molecule target 1
t2c1=1; %mass target atom target 2
t2c2=1; %mass reactive molecule target 2

q=1.6*10^-19; %electron charge (C)

%Compound Fractions---------------------------------
C1=0.5*(O1/M1); % This is done to re-calculated the required oxygen flux needed to form 1 molecule of compound, original BERG assumption is 1:1
C2=0.5*(O2/M2);

%Ambient conditions and constants-------------------
k=1.4*10^-23; %boltzmann's const (J/K)
ma=RGmass/1000; %weight of reactive species O (kg)
av=6.022*10^23; %avogadro's (atoms/mol)
m = ma/av; % atomic mass (kg)
pi = 3.14159;
a2sccm = 1/((7.45*10^-7)*(av)); % atoms/sec to sccm
m2sccm = 592; % m^3/s to sccm

% Gas calculations-------------------------------------
F = P*((2*k*T*pi*m)^(-1/2)); % surface O flux (#/m^2*s)
F1 = F*C1;
F2 = F*C2;
t1c1 = 1; % mass target atom target 1
t1c2 = 1; % mass reactive molecule target 1
t2c1 = 1; % mass target atom target 2
t2c2 = 1; % mass reactive molecule target 2
n1 = 2;
n2 = 2;

for i = 1:length(P);
    Ot1(i) = (2*a1*F1(i))/(2*a1*F1(i) + ((J1/q)*Yc1)); % theta T for
target surface compound fraction on T1
    Ot2(i) = (2*a2*F2(i))/(2*a2*F2(i) + ((J2/q)*Yc2)); % theta T for
target surface compound fraction on T2
    Fc1(i) = (J1/q)*Yc1*Ot1(i)*At1;
    Fc2(i) = (J2/q)*Yc2*Ot2(i)*At2;
    Fo1(i) = (J1/q)*Yc1*Ot1(i)*At1;
    Fo2(i) = (J2/q)*Yc2*Ot2(i)*At2;
    Fm1(i) = (J1/q)*Yc1*(1-Ot1(i))*At1;
    Fm2(i) = (J2/q)*Yc2*(1-Ot2(i))*At2;
    T1(i) = (J1/q)*At1*((Ym1*(1-Oc1(i)))+(Yc1*Ot1(i)));
    T2(i) = (J2/q)*At2*((Ym2*(1-Oc2(i)))+(Yc2*Ot2(i)));
end

y(i) = (T1(i))/(T1(i)+T2(i)); % Amount of target atoms sputtered
Oc1(i) = 2*Ac*C1^2*P(i)^2*a1^2*n1*q^2 +
2*Ac*C1*J1*P(i)*Yc1*a1*g*(2*pi*T*k*m)^(-1/2) +
At1*C1*J1*P(i)*Yc1*a1*n1*g*(2*pi*T*k*m)^(-1/2))/(2*Ac*C1^2*P(i)^2*a1^2*n1*q^2 +
2*pi*At1*J1^2*T*Yc1^2*k*m +
2*Ac*C1*J1*P(i)*Yc1*a1*g*(2*pi*T*k*m)^(-1/2) +
At1*C1*J1*P(i)*Yc1*a1*n1*g*(2*pi*T*k*m)^(-1/2));
Oc2(i) = 2*Ac*C2^2*P(i)^2*a2^2*n2*q^2 +
2*Ac*C2*J2*P(i)*Yc2*a2*g*(2*pi*T*k*m)^(-1/2) +
At2*C2*J2*P(i)*Yc2*a2*n2*g*(2*pi*T*k*m)^(-1/2))/(2*Ac*C2^2*P(i)^2*a2^2*n2*q^2 +
2*pi*At2*J2^2*T*Yc2^2*k*m +
2*Ac*C2*J2*P(i)*Yc2*a2*g*(2*pi*T*k*m)^(-1/2) +
At2*C2*J2*P(i)*Yc2*a2*n2*g*(2*pi*T*k*m)^(-1/2));
D1(i) = t1c1*(T1(i)*(1-Oc1(i)))+(t1c2*T1(i)*Oc1(i)); % deposition rate
at collector surface from T1
D2(i) = t2c1*(T2(i)*(1-Oc2(i)))+(t2c2*T2(i)*Oc2(i)); % deposition rate
at collector surface from T2
D(i) = D1(i)+D2(i); % Total Deposition Rate (atoms/s)
Qt1(i) = F1(i)*a1*(1-Ot1(i))*At1;
Qt2(i) = F2(i)*a2*At2*(1-Ot2(i));
\[ Q_{c1}(i) = F_1(i) * a_1 * y(i) * A_c * (1 - O_{c1}(i)) \]
\[ Q_{c2}(i) = F_2(i) * a_2 * A_c * (1 - y(i)) * (1 - O_{c2}(i)) \]
\[ Q_t(i) = Q_{t1}(i) + Q_{t2}(i) \]; % reactive gas uptake by target compound formation
\[ Q_c(i) = Q_{c1}(i) + Q_{c2}(i) \]; % reactive gas uptake by substrate compound formation
\[ Q_p(i) = S * P(i) \]; % reactive gas uptake by pumping system \((m^3/s)\)

\[ Qt_{1n} = Qt_{1} * a_2 \text{sccm} \]
\[ Qt_{2n} = Qt_{2} * a_2 \text{sccm} \]
\[ Qc_{1n} = Qc_{1} * a_2 \text{sccm} \]
\[ Qc_{2n} = Qc_{2} * a_2 \text{sccm} \]
\[ Q_{tn} = Qt * a_2 \text{sccm} \]
\[ Q_{cn} = Qc * a_2 \text{sccm} \]
\[ Q_{pn} = Qp * m2 \text{sccm} \]
\[ Qt_{otn} = Qt_{tn} + Qc_{tn} + Qp_{n} \]

\[ \text{Flow} = \text{str2double(get(handles.Flow,'String'))} \]
\[ \text{OcIndex} = \text{find}(Qt_{otn} > (\text{Flow} - 0.3) \; \& \; Qt_{otn} < (\text{Flow} + 0.3)) \]
\[ \text{Index} = \text{round(median(OcIndex))} \]
\[ PVal = P_1(\text{Index}) \]
\[ %OcVal1 = O_{c1}(\text{Index}) \]
\[ %OcVal2 = O_{c2}(\text{Index}) \]
\[ %VS = OcVal1 * (2 * (O_1/M_1)) \]
\[ %VS2 = OcVal2 * (2 * (O_2/M_2)) \]
\[ \text{set(handles.VS,'String',PVal)} \]
\[ \% \text{set(handles.VS2,'String',VS2)} \]

\[ F_{m1xx} = F_{m1}/av; \; \% \text{mols Ge} \]
\[ F_{m2xx} = F_{m2}/av; \; \% \text{mols Mo} \]
\[ F_{c1xx} = F_{c1}/av; \; \% \text{mols GeO}_2 \]
\[ F_{c2xx} = F_{c1}/av; \; \% \text{mols MoO}_3 \]
\[ F_{o1xx} = F_{o1}/av; \; \% \text{mols O} \]
\[ F_{o2xx} = F_{o2}/av; \; \% \text{mols O} \]
\[ F_{txx} = F_{o1xx} + F_{o2xx} \]
\[ ARR_1 = 2 * O_1/O_{t1}; \% \text{Arrival rate ratio of O:Ge} \]
\[ ARR_2 = 2 * O_2/O_{t2}; \% \text{Arrival rate ratio of O:Mo} \]

\[ \text{ARR} = [Qt_{otn}', P_1', ARR_1', ARR_2', y', O_{c1}', O_{c2}', O_{t1}', O_{t2}', Qt_{1n}', Qt_{2n}', Qc_{1n}', Qc_{2n}', Qt_{tn}', Qc_{tn}', Qp_{n}'] \]
\[ \text{VALENCE} = [Qt_{otn}', ARR_1', ARR_2'] \]
\[ \text{OCx} = [Qt_{otn}', O_{c1}', O_{t1}', O_{c2}', O_{t2}'] \]
\[ \text{xlswrite('ARR.xlsx',ARR)} \]
\[ \text{xlswrite('VALENCE.xlsx',VALENCE)} \]
\[ \text{xlswrite('OC.xlsx',OCx)} \]

\[ O_{c1prime} = \text{diff}(O_{c1}.*y) \]
\[ Q_{new} = Qt_{otn}(1:length(O_{c1prime})) \]
\[ O_{c1DP} = \text{diff}(O_{c1prime}) \]
\[ Q_{newnew} = Qt_{otn}(1:length(O_{c1DP})) \]
\[ O_{c2prime} = \text{diff}(O_{c2}.*(1-y)) \]
Oc2DP = \text{diff}(Oc2prime);

set(handles.axes1,'NextPlot','add');
set(handles.axes1,'XLimMode','manual');
set(handles.axes1,'XLim',[0,max(Qtotn)]);

set(handles.axes2,'NextPlot','add');
set(handles.axes2,'YLimMode','manual');
set(handles.axes2,'YLim',[0,1]);
set(handles.axes2,'XLimMode','manual');
set(handles.axes2,'XLim',[0,max(Qtotn)]);

set(handles.axes3,'NextPlot','add');
set(handles.axes3,'XLimMode','manual');
set(handles.axes3,'XLim',[0,max(Qtotn)]);

set(handles.axes4,'NextPlot','add');
set(handles.axes4,'XLimMode','manual');
set(handles.axes4,'XLim',[0,max(Qtotn)]);

set(handles.axes5,'NextPlot','add');
set(handles.axes5,'XLimMode','manual');
set(handles.axes5,'XLim',[0,max(Qtotn)]);

hold all
set(get(handles.axes1, 'XLabel'), 'String', 'O2 Flow Rate (sccm)')
set(get(handles.axes1, 'YLabel'), 'String', 'O2 Partial Pressure (mTorr)')
plot(handles.axes1, Qtotn, P1, 'r')
hold off

hold all
set(get(handles.axes2, 'XLabel'), 'String', 'O2 Flow Rate (sccm)')
set(get(handles.axes2, 'YLabel'), 'String', 'Fraction of Material 1, y')
plot(handles.axes2, Qtotn, y, 'r')
hold off

hold all
set(get(handles.axes3, 'XLabel'), 'String', 'O2 Flow Rate (sccm)')
set(get(handles.axes3, 'YLabel'), 'String', 'Valence State Ge (r) Mo (b)')
plot(handles.axes3, Qtotn, ARR1, 'r')
plot(handles.axes3,Qtotn,ARR2,'b')
hold off

hold all
set(get(handles.axes4, 'XLabel'), 'String', 'O2 Flow Rate (sccm)')
set(get(handles.axes4, 'YLabel'), 'String', 'Qt1(r) Qt2(b) Qc1(g)
Qc2(m) Qp(c)')
plot(handles.axes4,Qtotn,Qt1n,'r')
plot(handles.axes4,Qtotn,Qt2n,'b')
plot(handles.axes4,Qtotn,Qc1n,'g')
plot(handles.axes4,Qtotn,Qc2n,'m')
plot(handles.axes4,Qtotn,Qpn,'c')
hold off

hold all
set(get(handles.axes5, 'XLabel'), 'String', 'O2 Flow Rate (sccm)')
set(get(handles.axes5, 'YLabel'), 'String', 'O2 Removal Rate (sccm)')
plot(handles.axes5,Qtotn,Qtn,'r')
plot(handles.axes5,Qtotn,Qcn,'b')
plot(handles.axes5,Qtotn,Qpn,'k')
hold off

%  --- Executes during object creation, after setting all properties.
function pushbutton1_CreateFcn(hObject, eventdata, handles)
% hObject    handle to pushbutton1 (see GCBO)
% eventdata  reserved - to be defined in x5 future version of MATLAB
% handles    empty - handles not created until after all CreateFcns
called
%Reactive gas partial pressure%

%  --- Executes during object creation, after setting all properties.
function x3_CreateFcn(hObject, eventdata, handles)
% hObject    handle to x3 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns
called

%  --- Executes during object creation, after setting all properties.
function axes3_CreateFcn(hObject, eventdata, handles)
% hObject    handle to axes3 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns
called

%  Hint: place code in OpeningFcn to populate axes3

%  --- Executes on button press in pushbutton3.
function pushbutton3_Callback(hObject, eventdata, handles)
% hObject    handle to pushbutton3 (see GCBO)
cla(handles.axes1,'reset');
cla(handles.axes2,'reset');
cla(handles.axes3,'reset');
cla(handles.axes4,'reset');
cla(handles.axes5,'reset');

set(handles.axes1,'NextPlot','add');
set(handles.axes2,'NextPlot','add');
set(handles.axes3,'NextPlot','add');
set(handles.axes4,'NextPlot','add');
set(handles.axes5,'NextPlot','add');

function Flow_Callback(hObject, eventdata, handles)

% --- Executes during object creation, after setting all properties.
function Flow_CreateFcn(hObject, eventdata, handles)

% --- Executes during object creation, after setting all properties.
function RG_Callback(hObject, eventdata, handles)

% --- Executes during object creation, after setting all properties.
function RG_CreateFcn(hObject, eventdata, handles)
  hObject    handle to RG (see GCBO)
  eventdata   reserved - to be defined in a future version of MATLAB
  handles     empty - handles not created until after all CreateFcns called

  % Hint: edit controls usually have a white background on Windows.
  %       See ISPC and COMPUTER.
  if ispc && isequal(get(hObject,'BackgroundColor'),
                  get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor','white');
  end

function Yc2_Callback(hObject, eventdata, handles)
  hObject    handle to Yc2 (see GCBO)
  eventdata   reserved - to be defined in a future version of MATLAB
  handles     structure with handles and user data (see GUIDATA)

  % Hints: get(hObject,'String') returns contents of Yc2 as text
  %        str2double(get(hObject,'String')) returns contents of Yc2 as a double

  % --- Executes during object creation, after setting all properties.
  function Yc2_CreateFcn(hObject, eventdata, handles)
  hObject    handle to Yc2 (see GCBO)
  eventdata   reserved - to be defined in a future version of MATLAB
  handles     empty - handles not created until after all CreateFcns called

  % Hint: edit controls usually have a white background on Windows.
  %       See ISPC and COMPUTER.
  if ispc && isequal(get(hObject,'BackgroundColor'),
                  get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor','white');
  end

function Ym2_Callback(hObject, eventdata, handles)
  hObject    handle to Ym2 (see GCBO)
  eventdata   reserved - to be defined in a future version of MATLAB
  handles     structure with handles and user data (see GUIDATA)

  % Hints: get(hObject,'String') returns contents of Ym2 as text
  %        str2double(get(hObject,'String')) returns contents of Ym2 as a double

  % --- Executes during object creation, after setting all properties.
  function Ym2_CreateFcn(hObject, eventdata, handles)
  hObject    handle to Ym2 (see GCBO)
  eventdata   reserved - to be defined in a future version of MATLAB
  handles     structure with handles and user data (see GUIDATA)

  % Hint: edit controls usually have a white background on Windows.
  %       See ISPC and COMPUTER.
  if ispc && isequal(get(hObject,'BackgroundColor'),
                  get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor','white');
  end
% eventdata    reserved - to be defined in a future version of MATLAB
% handles      empty - handles not created until after all CreateFcns
called

% Hint: edit controls usually have a white background on Windows.
%       See ISPC and COMPUTER.
if ispc && isequal(get(hObject,'BackgroundColor'),
               get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor','white');
end

function At2_Callback(hObject, eventdata, handles)
% hObject    handle to At2 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'String') returns contents of At2 as text
%        str2double(get(hObject,'String')) returns contents of At2 as a
double

% --- Executes during object creation, after setting all properties.
function At2_CreateFcn(hObject, eventdata, handles)
% hObject    handle to At2 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns
called

% Hint: edit controls usually have a white background on Windows.
%       See ISPC and COMPUTER.
if ispc && isequal(get(hObject,'BackgroundColor'),
               get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor','white');
end

function a2_Callback(hObject, eventdata, handles)
% hObject    handle to a2 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'String') returns contents of a2 as text
%        str2double(get(hObject,'String')) returns contents of a2 as a
double

% --- Executes during object creation, after setting all properties.
function a2_CreateFcn(hObject, eventdata, handles)
% hObject    handle to a2 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns
called
% handles    empty - handles not created until after all CreateFcns
called

% Hint: edit controls usually have a white background on Windows.
%       See ISPC and COMPUTER.
if ispc && isequal(get(hObject,'BackgroundColor'),
    get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor','white');
end

function I2_Callback(hObject, eventdata, handles)
    % hObject    handle to I2 (see GCBO)
    % eventdata  reserved - to be defined in a future version of MATLAB
    % handles    structure with handles and user data (see GUIDATA)
    % Hints: get(hObject,'String') returns contents of I2 as text
    %        str2double(get(hObject,'String')) returns contents of I2 as a
double

    % --- Executes during object creation, after setting all properties.
    function I2_CreateFcn(hObject, eventdata, handles)
        % hObject    handle to I2 (see GCBO)
        % eventdata  reserved - to be defined in a future version of MATLAB
        % handles    empty - handles not created until after all CreateFcns
called
        % Hint: edit controls usually have a white background on Windows.
        %       See ISPC and COMPUTER.
        if ispc && isequal(get(hObject,'BackgroundColor'),
            get(0,'defaultUicontrolBackgroundColor'))
            set(hObject,'BackgroundColor','white');
        end

    function M2_Callback(hObject, eventdata, handles)
        % hObject    handle to M2 (see GCBO)
        % eventdata  reserved - to be defined in a future version of MATLAB
        % handles    structure with handles and user data (see GUIDATA)
        % Hints: get(hObject,'String') returns contents of M2 as text
        %        str2double(get(hObject,'String')) returns contents of M2 as a
double

        % --- Executes during object creation, after setting all properties.
        function M2_CreateFcn(hObject, eventdata, handles)
            % hObject    handle to M2 (see GCBO)
            % eventdata  reserved - to be defined in a future version of MATLAB
            % handles    empty - handles not created until after all CreateFcns
called

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function O2_Callback(hObject, eventdata, handles)
% hObject    handle to O2 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'String') returns contents of O2 as text
%       str2double(get(hObject,'String')) returns contents of O2 as a
double

% --- Executes during object creation, after setting all properties.
function O2_CreateFcn(hObject, eventdata, handles)
% hObject    handle to O2 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns
called

% Hint: edit controls usually have a white background on Windows.
%       See ISPC and COMPUTER.
if ispc && isequal(get(hObject,'BackgroundColor'),
         get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor','white');
end

% --- Executes on button press in pushbutton7.
function pushbutton7_Callback(hObject, eventdata, handles)
% hObject    handle to pushbutton7 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

P1=0:0.0005:3; %reactive gas partial pressure mTorr
P=P1*0.133; %reactive gas pressure Pa
S1=str2double(get(handles.S1,'String'));
S=S1/1000; %m^3/s
%1sccm=7.4*10^-7 moles/second
%1mol=22.4 liters

%Target 1 conditions-----------------------------------
Yc1=str2double(get(handles.Yc,'String'));%compound sputter yield
Ym1=str2double(get(handles.Ym,'String')); %Target sputter yield
At1=str2double(get(handles.At,'String')); %Target Area (m^2)
a1=str2double(get(handles.a,'String')); %sticking coeff
I1=str2double(get(handles.I,'String')); %current (C/s)
M1=str2double(get(handles.M,'String')); %Metal
O1=str2double(get(handles.O,'String')); %Oxygen
\[ J_1 = \frac{I_1}{A_{t1}}; \quad \text{electron flux } C/m^2*s \]

\[ Y_{c2} = \text{str2double(get(handles.Yc2,'String'))}; \quad \text{compound sputter yield} \]
\[ Y_{m2} = \text{str2double(get(handles.Ym2,'String'))}; \quad \text{Target sputter yield} \]
\[ A_{t2} = \text{str2double(get(handles.At2,'String'))}; \quad \text{Target Area} \ (m^2) \]
\[ a_2 = \text{str2double(get(handles.a2,'String'))}; \quad \text{sticking coeff} \]
\[ I_2 = \text{str2double(get(handles.I2,'String'))}; \quad \text{current} \ (C/s) \]
\[ M_2 = \text{str2double(get(handles.M2,'String'))}; \quad \text{Metal} \]
\[ O_2 = \text{str2double(get(handles.O2,'String'))}; \quad \text{Oxygen} \]
\[ J_2 = \frac{I_2}{A_{t2}}; \quad \text{electron flux } C/m^2*s \]

\[ T = \text{str2double(get(handles.T,'String'))}; \quad \text{Temperature} \]
\[ R_{Gmass} = \text{str2double(get(handles.RG,'String'))}; \quad \text{Mass} \]
\[ A_c = \text{str2double(get(handles.Ac,'String'))}; \quad \text{collector (substrate area)} \ (m^2) \]

Current state = get(handles.CurrentRB,'Value');
if Current state == get(handles.CurrentRB,'Max')
    \[ I_1 = \text{linspace(0,2,length(P1))}; \quad \text{electron flux } C/m^2*s \]
    \[ J_1 = \frac{I_1}{A_{t1}}; \quad \text{electron flux } C/m^2*s \]
    \[ I_2 = \text{linspace(0,2,length(P1))}; \quad \text{electron flux } C/m^2*s \]
    \[ J_2 = \frac{I_2}{A_{t2}}; \quad \text{electron flux } C/m^2*s \]
elseif button_state1 == get(hObject,'Min')
end

t_{1c1} = 1; \quad \text{mass target atom target 1} 
\]
\[ t_{1c2} = 1; \quad \text{mass reactive molecule target 1} \]
\[ t_{2c1} = 1; \quad \text{mass target atom target 2} \]
\[ t_{2c2} = 1; \quad \text{mass reactive molecule target 2} \]
\[ q = 1.6*10^{-19}; \quad \text{electron charge} \ (C) \]

% Compound Fractions----------------------------------
\[ C_1 = 0.5*(O_1/M_1); \quad \text{This is done to re-calculated the required oxygen} \]
\[ \text{flux needed to form 1 molecule of compound, original BERG assumption is} \]
\[ 1:1; \]
\[ C_2 = 0.5*(O_2/M_2); \]

% Ambient conditions and constants--------------------------
\[ k = 1.4*10^{-23}; \quad \text{boltzmann's const} \ (J/K) \]
\[ m_{a} = R_{Gmass}/1000; \quad \text{weight of reactive species O} \ (kg) \]
\[ a_v = 6.022*10^{23}; \quad \text{avogadro's} \ (\text{atoms/mol}) \]
\[ m = m_{a}/a_v; \quad \text{atomic mass} \ (kg) \]
\[ \pi = 3.14159; \]
\[ a_{2	ext{sccm}} = 1/((7.45*10^{-7})*(a_v)); \quad \text{atoms/sec to sccm} \]
\[ m_{2	ext{sccm}} = 592; \quad \text{m^3/s to sccm} \]
% Gas calculations-------------------------------------
P=P*((2*k*T*pi*m)^(-1/2)); % surface O flux (#/m^2*s)
P1=P*C1;
P2=P*C2;
t1c1=1; % mass target atom target 1
t1c2=1; % mass reactive molecule target 1
t2c1=1; % mass target atom target 2
t2c2=1; % mass reactive molecule target 2
n1=2;
n2=2;

for i=1:length(P);
    for j=i;
    Ot1(i)=(2*a1*F1(i))/((2*a1*F1(i))+((J1(j)/q)*Yc1)); % theta T for target surface compound fraction on T1
    Ot2(i)=(2*a2*F2(i))/((2*a2*F2(i))+((J2(j)/q)*Yc2)); % theta T for target surface compound fraction on T2
    Pc1(i)=(J1(j)/q)*Yc1*Ot1(i)*At1;
Pc2(i)=(J2(j)/q)*Yc2*Ot2(i)*At2;
    Fm1(i)=(J1(j)/q)*Yc1*(1-Ot1(i))*At1;
    Fm2(i)=(J2(j)/q)*Yc2*(1-Ot2(i))*At2;
    T1(i)=(J1(j)/q)*At1*(((Ym1*(1-Ot1(i)))+(Yc1*Ot1(i)))); % Amount of target atoms sputtered
    T2(i)=(J2(j)/q)*At2*(((Ym2*(1-Ot2(i)))+(Yc2*Ot2(i)))); % Amount of target atoms sputtered
    y(i)=(T1(i))/(T1(i)+T2(i)); % Amount of target one material on substrate

% Oc1(i)=(2*Ac*C1^2*P(i)^2*a1^2*n1*q^2 + 2*Ac*C1*J1*P(i)*Yc1*a1*q*(2*pi*T*k*m)^(1/2) + At1*C1*J1*P(i)*Yc1*a1*n1*q*(2*pi*T*k*m)^(1/2))/(2*Ac*C1^2*P(i)^2*a1^2*n1*q^2 + 2*pi*At1*J1*J1*T*Yc1^2*k*m + 2*Ac*C1*J1*P(i)*Yc1*a1*q*(2*pi*T*k*m)^(1/2) + At1*C1*J1*P(i)*Yc1*a1*n1*q*(2*pi*T*k*m)^(1/2));
% Oc2(i)=(2*Ac*C2^2*P(i)^2*a2^2*n2*q^2 + 2*Ac*C2*J2*P(i)*Yc2*a2*q*(2*pi*T*k*m)^(1/2) + At2*C2*J2*P(i)*Yc2*a2*n2*q*(2*pi*T*k*m)^(1/2))/(2*Ac*C2^2*P(i)^2*a2^2*n2*q^2 + 2*pi*At2*J2*J2*T*Yc2^2*k*m + 2*Ac*C2*J2*P(i)*Yc2*a2*q*(2*pi*T*k*m)^(1/2) + At2*C2*J2*P(i)*Yc2*a2*n2*q*(2*pi*T*k*m)^(1/2));
% D1(i)=t1c1*((T1(i)*(1-Oc1(i)))+(t1c2*T1(i)*Oc1(i)));
% D2(i)=t2c1*((T2(i)*(1-Oc2(i)))+(t2c2*T2(i)*Oc2(i)));
% D(i)=D1(i)+D2(i); % Total Deposition Rate (atoms/s)
% Qt1(i)=F1(i)*a1*(1-Ot1(i))*At1;
% Qt2(i)=F2(i)*a2*At2*(1-Ot2(i));
% Qc1(i)=F1(i)*a1*y(i)*Ac*(1-Oc1(i));
% Qc2(i)=F2(i)*a2*Ac*(1-y(i))*(1-Oc2(i));
% Qt(i)=Qt1(i)+Qt2(i); % reactive gas uptake by target compound formation
% Qc(i)=Qc1(i)+Qc2(i); % reactive gas uptake by substrate compound formation
\% Qp(i)=S*P(i); \%reactive gas uptake by pumping system (m^3/s)
end
end

T1

\% --- Executes on button press in CurrentRB.
function CurrentRB_Callback(hObject, eventdata, handles)
\% hObject    handle to CurrentRB (see GCBO)
\% eventdata  reserved - to be defined in a future version of MATLAB
\% handles    structure with handles and user data (see GUIDATA)

\% Hint: get(hObject,'Value') returns toggle state of CurrentRB

\% --- Executes on button press in SBR.
function SBR_Callback(hObject, eventdata, handles)
\% hObject    handle to SBR (see GCBO)
\% eventdata  reserved - to be defined in a future version of MATLAB
\% handles    structure with handles and user data (see GUIDATA)

\% Hint: get(hObject,'Value') returns toggle state of SBR

\% --- Executes on button press in TBR.
function TBR_Callback(hObject, eventdata, handles)
\% hObject    handle to TBR (see GCBO)
\% eventdata  reserved - to be defined in a future version of MATLAB
\% handles    structure with handles and user data (see GUIDATA)

\% Hint: get(hObject,'Value') returns toggle state of TBR

\% --- Executes on button press in radiobutton5.
function radiobutton5_Callback(hObject, eventdata, handles)
\% hObject    handle to radiobutton5 (see GCBO)
\% eventdata  reserved - to be defined in a future version of MATLAB
\% handles    structure with handles and user data (see GUIDATA)

\% Hint: get(hObject,'Value') returns toggle state of radiobutton5

\% --- Executes on button press in Select.
function Select_Callback(hObject, eventdata, handles)
\% hObject    handle to Select (see GCBO)
\% eventdata  reserved - to be defined in a future version of MATLAB
\% handles    structure with handles and user data (see GUIDATA)

[x,y]=ginput(1);
set(handles.xpick,'String',x);
set(handles.ypick,'String',y);

function Yo1_Callback(hObject, eventdata, handles)
    % hObject    handle to Yo1 (see GCBO)
    % eventdata  reserved - to be defined in a future version of MATLAB
    % handles    structure with handles and user data (see GUIDATA)
    % Hints: get(hObject,'String') returns contents of Yo1 as text
    %        str2double(get(hObject,'String')) returns contents of Yo1 as a double

    % --- Executes during object creation, after setting all properties.
    function Yo1_CreateFcn(hObject, eventdata, handles)
        % hObject    handle to Yo1 (see GCBO)
        % eventdata  reserved - to be defined in a future version of MATLAB
        % handles    empty - handles not created until after all CreateFcns called
        % Hint: edit controls usually have a white background on Windows.
        %       See ISPC and COMPUTER.
        if ispc && isequal(get(hObject,'BackgroundColor'),
                         get(0,'defaultUicontrolBackgroundColor'))
            set(hObject,'BackgroundColor','white');
        end

function Yo2_Callback(hObject, eventdata, handles)
    % hObject    handle to Yo2 (see GCBO)
    % eventdata  reserved - to be defined in a future version of MATLAB
    % handles    structure with handles and user data (see GUIDATA)
    % Hints: get(hObject,'String') returns contents of Yo2 as text
    %        str2double(get(hObject,'String')) returns contents of Yo2 as a double

    % --- Executes during object creation, after setting all properties.
    function Yo2_CreateFcn(hObject, eventdata, handles)
        % hObject    handle to Yo2 (see GCBO)
        % eventdata  reserved - to be defined in a future version of MATLAB
        % handles    empty - handles not created until after all CreateFcns called
        % Hint: edit controls usually have a white background on Windows.
        %       See ISPC and COMPUTER.
        if ispc && isequal(get(hObject,'BackgroundColor'),
                         get(0,'defaultUicontrolBackgroundColor'))
            set(hObject,'BackgroundColor','white');
        end
% --- Executes during object creation, after setting all properties.
function axes2_CreateFcn(hObject, eventdata, handles)
% hObject    handle to axes2 (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns
called

% Hint: place code in OpeningFcn to populate axes2