HYBRID CO-DEPOSITION OF MIXED-VALENT
MOLYBDENUM-GERMANIUM OXIDES (MoxgEYrZ):
A ROUTE TO TUNABLE OPTICAL TRANSMISSION
(POSTPRINT)

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General Dynamics Information Technology

3 MARCH 2015
Interim Report

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UNITED STATES AIR
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MOLYBDENUM-GERMANIUM OXIDES (Mo\textsubscript{x}Ge\textsubscript{y}O\textsubscript{z}): A
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14. ABSTRACT (Maximum 200 words)
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15. SUBJECT TERMS
Magnetron sputtering, Ellipsometry, X-ray photoelectron spectroscopy, Mixed oxides, Germanium oxide, Molybdenum oxide

16. SECURITY CLASSIFICATION OF:

a. REPORT Unclassified
b. ABSTRACT Unclassified
c. THIS PAGE Unclassified
Hybrid co-deposition of mixed-valent molybdenum–germanium oxides (Mo$_x$Ge$_y$O$_z$): A route to tunable optical transmission

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ABSTRACT

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 load, stepped from settings of 300 to 380 V, resulted in films ranging from mixtures of transparent GeO$_2$ (Ge$^{2+}$) and MoO$_2$ (Mo$^{6+}$) to the introduction of various absorptive ionic species including Mo$^{5+}$, Mo$^{4+}$, Ge$^{2+}$ and Ge$^{0}$, 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. As deposited Mo$_x$Ge$_y$O$_z$ thin films grown using this method have been shown to have optical gap energies that are able to be tailored between 3.57 eV and 0.18 eV, spanning useful ranges for devices operating in the visible and near-infrared.

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, such as aluminum zinc oxide [1–3] and indium tin oxide [3–5], switchable electrochromic smart windows [6–8], flat panel displays [9–12], and optical coating designs requiring mixtures of high and low refractive index materials, such as rugate filters [13,14] and infrared reflectors [1]. While most of these applications require fully stoichiometric, transparent oxide mixtures, recent works exploring substoichiometric oxide systems have generated interest due to their unique absorptive properties [15–17]. Specifically, studies by Gil-Rostra et al. [15,17–19] have utilized reactive magnetron sputtering to tailor the visible absorption of substoichiometric transition metal oxides, including Ni [15], Co [15,19], Fe [15], Cu [15,18], 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 SiO$_2$ matrix [15,20–22]. 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 [23,24]. The ability to systematically leverage the visible absorption of thin film coatings has several advantages for the development of coatings for ophthalmic usage [17,19,25], photovoltaics [4,26–29], light emitting diode components [30–32], and plasmonics, providing a potential alternative to lossy metal-based configurations [33–35].

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 shell. Typically, the selection of the metallic species is limited to those transition metals and lanthanides that have unfill d and f electron shells, respectively, which give rise to visible absorption as a result of excitation energies ranging from ~1 to 3 eV ($\lambda$ ≈ 400–1240 nm) [23,24,36]. 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 adsorbing 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 MoO$_2$ (relative to MoO$_3$) and stoichiometric GeO$_2$ are very similar at room temperature, $\Delta H^\circ_{\text{MoO}_2} = -588 \text{ kJ/mol and } \Delta H^\circ_{\text{GeO}_2} = -580 \text{ kJ/mol}$ [37], a potential indicator that these two compounds can be deposited concurrently. In addition to MoO$_2$ (Mo$^{4+}$), the facile reduction of MoO$_3$ can lead to the formation of MoO$_3$ and the corresponding ionic species, Mo$^{3+}$ [38–40]. 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 depositing mixed oxides include the use of alloyed targets [41–45], affixing strips of various materials to the target surface [15,17–19], and co-deposition using multiple sources [46–49]. 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, which allows 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 [50–53]. Therefore, fine adjustments in the applied MPPMS power should be able to accurately control the oxygen partial pressure within the deposition chamber via chemisorption [50,54–57].

This work uses a scalable co-deposition method that allows for the precise control of oxygen partial pressure in order to achieve controlled variation in both the composition and chemical state of mixed MoxGeyOz thin films. This work also explores the reduction pathway of the oxide compounds present within the deposited films, and provides a detailed correlation between processing parameters, chemical properties and optical behavior. Finally, the methods outlined within this study are intended to serve as a template for the deposition and exploration of other substoichiometric mixed-oxide systems.

2. Experimental

2.1. Fabrication

MoxGeyOz films were deposited within a stainless steel high-vacuum chamber 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. Lesker Torus®) was equipped with a 50 mm germanium (Plasmaterials, 99.999% purity) sputter target. The second magnetron (Meivac MAK®) was equipped with a 50 mm molybdenum target (Plasmaterials, 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 Inc.) and 1.65 mm thick fused quartz (Machine Glass Specialists Inc.) were loaded into the chamber through a load-lock system. Substrates were placed upon 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. 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, 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 ($Q_\text{Ar}$) of 25 sccm using a mass flow controller. The pressure of the argon gas ($P_\text{Ar}$), measured using a capacitance manometer, was set at 1.33 Pa and maintained constant by locking the gate valve position. The static gate valve resulted in a constant pumping speed of approximately 32 L/s. $P_\text{Ar}$ was expected to be constant throughout all depositions, assuming a negligible amount of argon loss through ion implantation at the target surfaces. Once $P_\text{Ar}$ was stabilized at 1.33 Pa, oxygen (99.999%) was introduced through a separate mass flow controller. The oxygen partial pressure, $P_\text{O}_2$, was determined by subtracting $P_\text{Ar}$ from the total chamber working pressure $P_\text{Total}$. The oxygen flow rate ($Q_\text{O}_2$) was first stepped from 0 to 10 sccm, in 1 sccm increments. Adjustment of $Q_\text{O}_2$ 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 $Q_\text{O}_2$ was set to 6 sccm resulting in a total flow rate ($Q_\text{Total}$) of 31 sccm. Justification for the selection of $Q_\text{O}_2$ can be found in Section 3 below. 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 2Pulsar Axia 180 MPPMS 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 voltage loads ($U_\text{L}$) 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. [50]. The first stage of the pulse generated a low energy plasma discharge with a duration of 400 μs derived from a 20% micro-pulse 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 cathode 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 quartz witness samples for a total of 3 min, resulting in thicknesses ranging from 220 to 300 nm. In the case of samples prepared for X-ray reflectivity, the deposition time was held for 1 min to ensure an appropriate thickness ($\leq$ 100 nm).

2.2. Characterization

The composition, chemistry, optical properties, and structure of as-deposited MoxGeyOz thin films were studied using a combination of grazing incidence X-ray diffraction (GIXRD), X-ray reflectivity (XRR), X-ray photoelectron spectroscopy (XPS), spectroscopic ellipsometry (SE), and ultraviolet–visible-near-infrared optical spectrophotometry (UV–Vis–NIR).

Structural properties of the as-deposited MoxGeyOz 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 of films deposited on Si(100) wafers were taken within a 2θ range of 15–80° at a rate of 0.1/°. XRR scans were obtained for 2θ values between 0° and 60° with a step size of 0.005°. Raw XRR data were fit within 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. The presence of adventitious carbon is the result of atmospheric exposure during transportation from the deposition system to the analysis chamber. 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.

The optical properties of the Mo<sub>0</sub>Ge<sub>1</sub>O<sub>z</sub> films were evaluated using a J.A. Woollam VASE spectroscopic ellipsometer in both transmission (T) and SE modes over a wavelength range of 255–1700 nm (4.86–0.72 eV). A single model was used to simultaneously fit both transmitted intensity and variable angle SE data in order to ensure precise, unique solutions for the refractive index, extinction coefficient, and thickness of the absorbing thin films. Most importantly, the use of the VASE instrument’s transmission mode, measuring transmitted intensity at normal incidence through the film and substrate, allows for increased precision in determining the onset of absorption attributed to the optical band gap. 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 at angles of incidence of 50°, 55°, and 60°. The spectral refractive index (n(λ)), the extinction coefficient (κ(λ)), and the thickness of the films were calculated by simultaneously fitting raw T and SE data with a Kramers–Kronig consistent optical model, described in detail in Section 3.4. T data was weighted 2:1 versus SE data and the optical model was optimized in order to minimize the resulting mean squared error (MSE) through iterative adjustment of the fitting parameters using the Levenberg–Marquardt method, improving the fit quality. Fits with an MSE greater than 25 were rejected.

3. Results and discussion

3.1. Establishment of conditions

The oxygen partial pressure (P<sub>O</sub><sub>2</sub>), as a function of flow rate (Q<sub>O</sub><sub>2</sub>), was carefully monitored prior to deposition with both magnetron sources. As mentioned previously, the partial pressure of argon (P<sub>Ar</sub>) was set to 1.33 Pa and then oxygen was introduced into the deposition chamber. Pumping speeds were calculated by analyzing the working pressure as a function of Q<sub>O</sub><sub>2</sub> prior to plasma ignition in order to ensure no reduction in P<sub>O</sub><sub>2</sub> through oxide formation due to chemisorption. Using only the Ge source, a plot of (P<sub>O</sub><sub>2</sub>) versus Q<sub>O</sub><sub>2</sub> is shown in Fig. 1. The pumping speed (S = Q<sub>TOT</sub>/P<sub>TOT</sub>) attributed to each set of P<sub>TOT</sub> vs. Q<sub>TOT</sub> was calculated, resulting in an average rate of 32 L/s. P<sub>TOT</sub> was then evaluated as a function of Q<sub>O</sub><sub>2</sub> 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. As demonstrated in Fig. 1, the value of P<sub>O</sub><sub>2</sub> at Q<sub>O</sub><sub>2</sub> = 0.0 is 0 Pa, validating the assumption of constant argon pressure during sputtering. As Q<sub>O</sub><sub>2</sub> increases to 1 sccm, there is no change in P<sub>O</sub><sub>2</sub>, indicating that all available oxygen is effectively chemisorbed. Changes in P<sub>O</sub><sub>2</sub>, associated with the presence of gaseous oxygen, begin to arise at Q<sub>O</sub><sub>2</sub> ≥ 2 sccm. Increases in P<sub>O</sub><sub>2</sub> for 1 < Q<sub>O</sub><sub>2</sub> ≤ 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 Fig. 1; this commonly reported behavior is associated with the oxidation and reduction of the sputter target surface as reactive gas content is varied [55–57, 60–62]. At Q<sub>O</sub><sub>2</sub> values near 5 sccm and above, P<sub>O</sub><sub>2</sub> increases linearly at a rate proportional to the pumping speed of the system. The linear behavior of P<sub>O</sub><sub>2</sub> 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<sub>2</sub>. The goal of this work requires the initial deposition of transparent, dielectric GeO<sub>2</sub> and MoO<sub>3</sub>, followed by the incorporation of optically absorbing metal-oxide coordination complexes associated with substoichiometric oxide formation characteristic of transition mode sputtering [55–57,60–62]. 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 [50,54,63].

Havening identified the onset of target poisoning for germanium deposition, characterization of the P<sub>O</sub><sub>2</sub> vs. Q<sub>O</sub><sub>2</sub> behavior for the co-deposition from Ge and Mo targets was performed using Q<sub>O</sub><sub>2</sub> values of 4, 6, and 8 sccm. P<sub>TOT</sub> values corresponding to Q<sub>O</sub><sub>2</sub> = 4, 6, and 8 sccm were recorded as a function of U<sub>L</sub> applied to the molybdenum sputter source; note that the germanium source was operated concurrently at 100 W DC. A plot of P<sub>O</sub><sub>2</sub> vs. U<sub>L</sub> shown in Fig. 2, demonstrates significant differences in behavior for Q<sub>O</sub><sub>2</sub> values of 4, 6, and 8 sccm. As expected, P<sub>O</sub><sub>2</sub> values shown in Fig. 2 decrease as a function of increasing U<sub>L</sub> due to...
oxygen uptake associated with the additional molybdenum deposition flux. Based on the data in Fig. 2, the onset of the transition regime is demonstrated by the characteristic decrease in PO2 as a function of increasing UL.

The relatively flat behavior of PO2 at lower UL values is attributed to the inability to fully react with the excess oxygen present within the chamber, consistent with the poisoned regime. As UL increases, the pressure begins to decrease due to the higher levels of molybdenum deposition flux brought on by the augmentation of UL. Since UL is directly related to the magnitude of the discharge voltage, depicted in Fig. 3a, increases in UL are responsible for augmenting the kinetic energy of incident Ar+ ions responsible for sputtering. Therefore, further increases in UL lead to the reduction of oxides formed on the target surfaces, giving way to the onset of transition mode sputtering, as demonstrated by the decrease in PO2 and PTOT. Since UL is directly related to the magnitude of the discharge voltage, depicted in Fig. 3a, increases in UL are responsible for augmenting the kinetic energy of incident Ar+ ions responsible for sputtering. Therefore, further increases in UL lead to the reduction of oxides formed on the target surfaces, giving way to the onset of transition mode sputtering, as demonstrated by the decrease in PO2 and PTOT. As shown in Fig. 3a, 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 PO2 of 0.00 Pa, corresponding to PAr = 1.33 Pa. The onset of gettering is clear for QO2 = 4 sccm, at 330 V (Fig. 2), while QO2 values of 6 and 8 sccm correspond to PO2 levels that are unable to be fully chemisorbed by the deposition flux even at UL = 380 V. The resulting augmentation of the molybdenum deposition flux is associated with both an increase in both discharge current (Fig. 3b) and photoemission attributed to excited molybdenum species (Mo I) (Fig. 3c). Current and voltage values for the Ge and Mo sputter sources can be found in Tables 1 and 2, respectively. Note, the UL value of 380 V corresponds to an average current of approximately 0.7 A; higher UL settings could not be used due to the thermal constraints of the magnetrons. The levels of PO2 for QO2 = 6 sccm are shown to have sufficient sensitivity to UL to allow for reduction of the oxygen content in the chamber, while still retaining stability over a wide range of partial pressures (Fig. 2). As a result of this analysis, QO2 = 6 sccm was selected for the deposition of MoxGeOy films.

### Table 1

<table>
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<tr>
<th>UL (V)</th>
<th>DCMS germanium</th>
<th>Voltage (V)</th>
<th>Current (I)</th>
<th>Power (W)</th>
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<td>0.190</td>
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<tr>
<td>310</td>
<td>523</td>
<td>0.190</td>
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<td>320</td>
<td>522</td>
<td>0.190</td>
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<td></td>
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<tr>
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<td>506</td>
<td>0.196</td>
<td>99.2</td>
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3.2. Structure and morphology

Measurement of the crystallinity of MoxGeOy thin films indicated that all films deposited were XRD amorphous, as evidenced by the presence of the lack of diffraction peaks as well as the broad amorphous humps shown in Fig. 4. Similar amorphous character has been reported by Mohamed et al. for sputter deposited MoO3, demonstrating broad amorphous humps with centroids moving from 2θ = 27° to 2θ = 38° as the oxygen partial pressure is decreased from 0.16 to 0.022 Pa [64].

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 [65–67], and incompatibility of mixing between the germanium and molybdenum oxide compounds [68,69]. 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 [15,17–19].

![Fig. 3. 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.](image-url)
XRR measurements were performed to probe the density, thickness, and roughness of the Mo₇Ge₅O₂₇ films deposited at UL values of 300 to 380 V. XRR is able to provide an estimation of the density based on the location of the critical angle (θc), below which, the total reflection of incident X-rays occurs [70]. In addition to density, film thickness can be calculated based on the period of oscillations known as Kiessig fringes [70]. 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 [70]. 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, comprised 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 [15,17–19]. Based on the data shown in Fig. 5, the behavior of the reflected X-ray intensity shows an increase in θc 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 Fig. 5. Roughness values remained relatively stable as a function of UL, varying between 0.5 and 2.0 nm, while calculated densities (Fig. 6) demonstrate a non-linear increase as a function of UL. Note that the calculated density rises from 3.2 to 6.4 g/cm³ as UL is increased from 300 to 380 V. The initial low density values, at 300 ≤ UL ≤ 350 can be attributed to the relatively high amount of residual oxygen present within the chamber (Fig. 2), resulting in the growth of fully oxidized

### Table 2

<table>
<thead>
<tr>
<th>UL (V)</th>
<th>MPPMS molybdenum</th>
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<tr>
<td>Peak voltage (V)</td>
<td>Peak current (I)</td>
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**Fig. 4.** Raw grazing incidence X-ray diffraction patterns from Mo₇Ge₅O₂₇ thin films for selected values of UL. Diffraction patterns are offset for clarity.

**Fig. 5.** Selected XRR measurements (black dotted line) and model calculations (semi-transparent red line) for determination of thickness, roughness, and density.

**Fig. 6.** Density measurements as a function of MPP capacitor bank voltage load (UL).
films. However, the densities of the oxygen-rich films within the 300 ≤ Ul ≤ 350 region are significantly lower than that of their bulk constituents [37,64,71–73]. The discrepancy between bulk densities for GeO2 and MoO3 and those of the as-deposited films can be attributed to no heating being 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 [65–67]. 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 Fig. 4. The increases in density obtained for higher values of Ul resulted from the growth of higher density, sub-stoichiometric compounds associated with the drop in PO2 at 350 ≤ Ul.

3.3. Measurement of MoxGeyOz composition and valence state

XPS survey scans, shown in Fig. 7 for Ul values of 300 and 380 V, were performed in order to determine the atomic concentrations of the constituents. The core level transitions used were O 1s, Mo 3d, Ge 2p3/2, and C 1s. Compositions from, and binding energies of, these transitions are included in Table 3. As demonstrated in Fig. 7, the concentrations of the constituent elements vary significantly for Ul values of 300 and 380 V. Films deposited at Ul = 300 V were found to contain approximately 3% C, 68% O, 4% Mo, and 25% Ge, while films deposited at Ul = 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 Ul values.

High energy resolution XPS measurements of the Ge 3d (Fig. 8) and Mo 3d (Fig. 9) transitions were acquired for Ul values from 300 to 580 V in addition to survey scans. Measurement and analysis of high energy resolution XPS spectra were conducted in order to gain understanding of the oxidation states present within the deposited films. XPS data for the Ge 3d (Fig. 8) and Mo 3d transitions (Fig. 9) indicate changes in oxidation states in response to the decreased levels of PO2 brought on by increases in Ul. Beginning with the Ge 3d transition, incremental changes in Ul from 300 to 370 V are associated with spectra centered at BE = 285 eV, consistent with published values for the Ge4+ cation associated with tetrahedral GeO2 [72,74]. As Ul is increased further, to 375 V, the evolution of the Ge5+ cation, attributed to the presence of trigonal planar GeO can be observed at BE = 31.0 eV in addition to the GeO2 [72,74,75]. Note, the trigonal planar arrangement of GeO is represented by increases in Ul. Beginning with the Ge 3d transition, incremental changes in Ul from 300 to 370 V are associated with spectra centered at BE = 32.8 eV, consistent with published values for the Ge4+ cation.

Table 3

<table>
<thead>
<tr>
<th>Ul (V)</th>
<th>C 1s Binding energy (eV)</th>
<th>O 1s Binding energy (eV)</th>
<th>Mo 3d Binding energy (eV)</th>
<th>Ge 2p3/2 Binding energy (eV)</th>
<th>at.%</th>
<th>at.%</th>
<th>at.%</th>
<th>at.%</th>
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<tbody>
<tr>
<td>300</td>
<td>285.1</td>
<td>3.4</td>
<td>532.3</td>
<td>67.7</td>
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<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>
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<td>330</td>
<td>284.9</td>
<td>7.2</td>
<td>532.9</td>
<td>67.7</td>
<td>232.9</td>
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<td>14.9</td>
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<td>350</td>
<td>285.2</td>
<td>9.5</td>
<td>532.4</td>
<td>65.4</td>
<td>232.4</td>
<td>8.6</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>
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<td>285.2</td>
<td>13.4</td>
<td>532.4</td>
<td>61.0</td>
<td>231.6</td>
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<td>375</td>
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<td>231.0</td>
<td>11.4</td>
<td>1220.6</td>
<td>16.9</td>
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<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>

Fig. 7. XPS survey scans for MoxGeyOz films deposited for Ul values of 380 V (top) and 300 V (bottom) spectra are offset for clarity. Ul = 380 V is associated with enhanced ratios of MoO.

Fig. 8. High energy resolution XPS measurements of the Ge 3d transition for several values of Ul. Note that spectra for Ul = 310 and 330 were omitted due to similarity with Ul = 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.
indicating the presence of the intermediate surface compound MoO$_2$. The concentration of Mo$^{5+}$, relative to Mo$^{6+}$, continues to increase from 15% to 85% as $U_L$ is increased from 340 to 360 V. Formation of the Mo$^{4+}$ cation (BE$_{3d5/2} = 229.2$ eV) occurs at $U_L > 360$ V, indicating the presence of tetrahedral MoO$_2$ in conjunction with MoO$_3$ and Mo$_2$O$_5$. Further increases in $U_L$ 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$^{5+}$ and Mo$^{6+}$. An average binding energy associated with the presence of the intermediate surface compound MoO$_2$ of 233.0 was measured for all values of $U_L$, with a maximum binding energy of 234.6 at $U_L = 370$ V and a minimum of 232.1 occurring at $U_L$ from 300 to 320 V, similar to coloration reported by Gil-Rostra et al. for mixed Mo$_x$Si$_y$O$_z$ thin films [15]. As $U_L$ is increased further, the films take on a yellow hue (Fig. 11d–g), showing sensitivity to the increasing proportion of the surface phase MoO$_2$. Subsequently, at $U_L$ values from 370 V to 380 V (Fig. 11h–l), 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.

### 3.4. Optical Characterization

The optical constants, $n$ and $k$, and deposition rates of the Mo$_x$Ge$_y$O$_z$ thin films were determined through measurement and simultaneous fitting of SE and T data. The model used within this work consists of a 1.65 mm quartz substrate, a general oscillator layer, and a Bruggeman effective medium layer, coupled to the general oscillator layer, consisting of 50% void fraction to account for the presence of surface roughness [59]. Raw data acquired through SE and T measurements were fit using a general oscillator model consisting of a Tauc–Lorentz oscillator (Eq. (1)) to account for the onset of the optical gap in the amorphous thin films and a Lorentz oscillator (Eq. (2)) to properly fit the observed absorption tail at energies beneath the optical gap [78,79]. For the film deposited at $U_L = 380$ V, one Tauc–Lorentz and two Lorentz oscillators were used in order to account for absorption features associated with the presence of elemental germanium and metallic molybdenum [78].

The effects of $U_L$ on both the coordination chemistry, and the relative concentrations of the compounds present, are shown in Fig. 10. Fig. 10 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.

$$e_2(E) = 2nk = \frac{AE_0C(E-E_o)^2}{(E^2-E_o^2)^2 + C^2E^2} \frac{1}{E}$$ \hspace{1cm} (1)

$$\bar{n}(\lambda)^2 = 1 + \sum_{j} \frac{A_j \lambda^2}{\lambda_j^2 - \lambda^2 + i B_0}$$ \hspace{1cm} (2)

In Eq. (1), $A$ and $C$ represent the amplitude and broadening terms of the Tauc–Lorentz oscillator, while $E$, $E_o$, and $E_i$ are the photon energy,
The parameters $A$, $B$, and $\lambda_0$ represent the amplitude, broadening, and centroid of the Lorentz oscillator (Eq. (2)) [59]. Utilization of the Tauc–Lorentz oscillator is highly advantageous due to its ability to directly calculate $E_g$. Overlays of selected models and experimentally measured $\Psi$ values at 50°, 55°, and 60° are shown in Fig. 12; associated transmission measurements are depicted in Fig. 13. A list of key fit parameters and model MSE values are shown in Table 4, note that the model MSE values are slightly elevated due to the simultaneous fitting of the SE and T data.

Film thicknesses and the corresponding deposition rates determined from XRR and SE measurements are shown in Fig. 14. Simultaneous modeling of SE and T data, and comparison with XRR thickness measurements, was performed in order to validate the fit quality, ensuring a unique solution for the thicknesses and optical constants. The thickness deposition rate shown in Fig. 14a indicates moderate change as a function of UL, varying between 72 and 96 nm/min. 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 Fig. 14b. Note that densities were calculated assuming a uniform thickness over an area of 1 cm$^2$. The data in Fig. 14b illustrates a non-linear increase in the mass deposition rate as a function of UL. The increased densification and associated 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 [56,57,80]. Higher applied voltages produce increased kinetic energies of the incident Ar$^+$ ions, resulting in more sputtered atoms per ion collision [56, 57,80]. 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.

The optical constants, $n$ and $k$, for the Mo$_x$Ge$_y$O$_z$ thin films are shown in Fig. 15a–b, respectively. The spectral behavior of both $n$ and $k$ indicates a dependence on the value of UL used for deposition. For $U_L \leq 330$ V, $n$ is relatively flat, ranging between 1.60 and 1.78 throughout the measured spectral region (380–1700 nm). A noticeable change in the dispersion, $n(\lambda)$, occurs at $U_L = 340$ V, wherein the value of $n$ varies from 1.65 in the near IR to 1.85 at 255 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) [64, 71, 81] to GeO$_2$ ($E_g = 5.6$–5.9) [75,82,83] as determined by XPS. As evidenced by Fig. 15, increases in $U_L$ from 300 to 340 V, lead to higher $n$ values, with $k$ values gradually increasing towards the UV region. While the growth of $k$ can be attributed to decreases in the optical gap energy, the spectral augmentation of $n$ is likely 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 (Fig. 6) and $n(\lambda)$ (Fig. 15a) is in line with the Lorentz–Lorenz relation [46,67]. $U_L$ 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 $U_L$.

The calculation of the $E_g$ values was performed by simultaneously modeling the SE and T data and extracting the $E_g$ term from the Tauc–Lorentz component of the general oscillator layer (Eq. (1)). $E_g$...
measurements were performed to determine the onset of inter-band 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<sub>x</sub>Ge<sub>y</sub>O<sub>z</sub> films, it would be difficult to fully parameterize the effect that each has upon the electronic structure of the films [84]. However, the combination of XRR, XPS, SE, and T measurements provides an adequate correlation between the optical and chemical properties of the films.

The chemical constituents, identified by XPS in Section 3.3, include GeO<sub>2</sub>, GeO, Ge, MoO<sub>3</sub>, Mo<sub>2</sub>O<sub>5</sub>, MoO<sub>2</sub>, and Mo. These compounds and elements have different electronic structures, namely, wide E<sub>g</sub> semiconductors in the case of GeO<sub>2</sub>, GeO [72,73,75] and MoO<sub>3</sub> [29,64,85,86], semiconducting Ge [87], and electrically conductive materials such as Mo and MoO<sub>2</sub> [39,77,88–91]. Published values for the band energies of each of the chemical constituents present are listed in Table 5. The VASE transmission plots, and overlaid model calculations, shown in Fig. 13 indicate large changes in the optical properties of the Mo<sub>x</sub>Ge<sub>y</sub>O<sub>z</sub> films as a function of U<sub>L</sub>.

### Table 4

Mean squared error (MSE), thickness, roughness, and E<sub>g</sub> values measured using variable angle spectroscopic ellipsometry.

<table>
<thead>
<tr>
<th>U&lt;sub&gt;L&lt;/sub&gt; (V)</th>
<th>Error (MSE)</th>
<th>Thickness (nm)</th>
<th>Roughness (nm)</th>
<th>E (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>9.76</td>
<td>251</td>
<td>3.3</td>
<td>3.57 ± 0.04</td>
</tr>
<tr>
<td>310</td>
<td>12.88</td>
<td>251</td>
<td>0.6</td>
<td>3.36 ± 0.05</td>
</tr>
<tr>
<td>320</td>
<td>22.58</td>
<td>267</td>
<td>3.5</td>
<td>3.35 ± 0.08</td>
</tr>
<tr>
<td>330</td>
<td>13.11</td>
<td>264</td>
<td>3.0</td>
<td>2.97 ± 0.04</td>
</tr>
<tr>
<td>340</td>
<td>19.54</td>
<td>271</td>
<td>2.9</td>
<td>1.61 ± 0.03</td>
</tr>
<tr>
<td>350</td>
<td>15.85</td>
<td>276</td>
<td>3.3</td>
<td>1.27 ± 0.05</td>
</tr>
<tr>
<td>360</td>
<td>17.98</td>
<td>277</td>
<td>3.8</td>
<td>0.84 ± 0.07</td>
</tr>
<tr>
<td>370</td>
<td>18.53</td>
<td>265</td>
<td>4.6</td>
<td>0.18 ± 0.02</td>
</tr>
<tr>
<td>375</td>
<td>20.84</td>
<td>290</td>
<td>6.9</td>
<td>0.00 ± 0.01</td>
</tr>
<tr>
<td>380</td>
<td>8.34</td>
<td>214</td>
<td>6.8</td>
<td>0.00 ± 0.45</td>
</tr>
</tbody>
</table>

Fig. 13. VASE transmission plots for all deposited films and associated model fits (dashed lines). Note the excellent fit quality in the regions near the band edge \( \lambda < 400 \text{ nm} \). Scales are individually adjusted to allow for assessment of fit quality.

Fig. 14. Deposition rates as calculated from XRR and SE analysis. a) Thickness deposition rates as a function of U<sub>L</sub>. b) Mass deposition rates as a function of U<sub>L</sub>. Deposition time for these samples was 1 min.
The onset of band-to-band absorption is easily identifiable by the precipitous drops in transmission shown in Fig. 13, and by the systematic increases in $k$ towards the UV region depicted by Fig. 15b. Given the high quality of the fitting within both Figs. 12 and 13, especially in the wavelength region encompassing the band edge, it is evident that the Tauc–Lorentz oscillator calculation provides an accurate estimation of $E_g$. Interestingly, the $E_g$ values for films deposited within the poisoned regime ($U_l \leq 330$ V) (Table 4) are significantly lower than values for bulk germanium oxide (Table 5) (5.9 $E_g$ ≤ 6) [72,73,75,83]; this is likely due to the presence of MoO$_3$ and is potential result of the formation of MoO$_3$ (Mo$^{6+}$) c o n - d u c t o r s. Similar complex bonding structures, involving oxygen sharing between octahedral metal oxides and tetrahedral oxides of both SiO$_2$ [15] and GeO$_2$ [92] have been reported for reactively sputtered mixed oxide compounds. When compared with XPS data, the gradual decrease in $E_g$ from 3.57 (±0.04) at $U_l = 300$ V to 2.97 eV (±0.04) at $U_l = 330$ V is associated with an 18% increase in MoO$_3$ (Mo$^{6+}$) content. Upon entering the transition regime (II), $E_g$ changes rapidly for $U_l$ values of 340, 350 and 360 V, corresponding to values of 1.61 (±0.03), 1.27 (±0.05), and 0.84 eV (±0.07), respectively. The large change observed in $E_g$ from 340–360 V indicates that $E_g$ is significantly affected by the 32% increase of the surface phase Mo$_2$O$_5$ (Mo$^{5+}$) and associated oxygen vacancies. Further increases in $U_l$ from 370 to 375 V are characterized by a decrease in $E_g$ from 0.18 (±0.02) to 0.00 eV (±0.01), respectively. This marked decrease in $E_g$ at 370 and 375 V is directly related to the presence of MoO$_2$ (Mo$^{4+}$) and, concurrently, GeO$_2$ (Ge$^{2+}$). An $E_g$ of 0.00 (±0.45) eV, was also found to occur at $U_l = 380$ 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 Fig. 10. Investigation of the relationship between $E_g$ and $U_l$ has indicated that increases in $U_l$ 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 Fig. 10. A detailed physical explanation of the changes in $E_g$, as a function of the processing parameter $U_l$, is presented and discussed in the next section.

### 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$_{O_2}$ as a result of increasing $U_l$. 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 was shown in Fig. 15b. 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 $U_l$ can be reached. As depicted in Figs. 10 and 16, 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, $E_g = 3.57$ eV (±0.04), deposited at a $U_l$ 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 [7]. 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 (pr) levels [7,38,93,94]. 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 $U_l$ is increased further, to 310 and 320 V, a slight blue–gray tint is

![Fig. 15. Plot of the refractive index (a) and extinction coefficient (b) as a function of wavelength for the different capacitor bank voltage load values ($U_l$).](image)

![Fig. 16. Calculated values of $E_g$ for $U_l$ 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.](image)

#### Table 5: List of published band gaps for selected oxides of germanium and molybdenum.

<table>
<thead>
<tr>
<th>Oxidation state</th>
<th>Compound</th>
<th>Band gap, $E_g$ (eV)</th>
<th>Reference no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge 0</td>
<td>Ge</td>
<td>0.67–0.88</td>
<td>[72,73,75]</td>
</tr>
<tr>
<td>Ge 2+</td>
<td>GeO$^+$</td>
<td>2.8–4.0</td>
<td>[75,95]</td>
</tr>
<tr>
<td>Ge 4+</td>
<td>GeO$_2$</td>
<td>5.9–6.1</td>
<td>[72,73,75,86]</td>
</tr>
<tr>
<td>Mo 0</td>
<td>Mo</td>
<td>0</td>
<td>[39,92–94]</td>
</tr>
<tr>
<td>Mo 4+</td>
<td>MoO$_2$</td>
<td>0</td>
<td>[39,92–94]</td>
</tr>
<tr>
<td>Mo 5+</td>
<td>MoO$_2$$^+$</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Mo 6+</td>
<td>MoO$_3$</td>
<td>2.7–3.2</td>
<td>[64,84,96,97]</td>
</tr>
</tbody>
</table>

a Band gaps are from numerical simulations.

b Note that MoO$_2$ is classified as a “surface phase” with no known bulk structure [38–40].
observed, corresponding to E_g values of 3.36 (±0.05) and 3.35 (±0.08) eV. Previous studies have observed blue coloration in slightly reduced MoO_3 films with oxygen vacancies, denoted as MoO_3−x [15,38,94]. 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 unoccupied t_2g band [73,38,94]. Increasing U_D to 330 V corresponds to films with an E_g of 2.97 (±0.04) eV, leading to a yellow tint associated with the increased Mo:Ge ratio. An E_g near 2.8 eV is near the lower bound of those reported for MoO_3 [29,64], and is related to absorption of blue light (λ < 440 eV), leading to a yellow coloration [36,95]. The yellow hue of the films persists, becoming more intense within the transition regime (II) for U_D values of 340 to 360 eV. Previous studies have observed blue coloration in slightly reduced PO_2 and E_g. The process

Furthermore, the presence, and relative amounts, of the different co-


doping levels in indirect semiconductors [84]. The slope, and magnitude

doing levels in indirect semiconductors [84]. The slope, and magnitude

doing levels in indirect semiconductors [84]. The slope, and magnitude

References


