Hybrid co-deposition of molybdenum doped niobium pentoxide ($\text{Nb}_x\text{Mo}_y\text{O}_z$) thin films

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Abstract

Mixed valent thin films, consisting of optically absorbing metallic cations within a dielectric matrix, possess a variety of optical and electronic properties that can be tailored through variation of dopant concentration and chemistry. This work details the reactive magnetron co-deposition of mixed valent $\text{Nb}_x\text{Mo}_y\text{O}_z$ thin films, systematically doped with optically absorbing Mo^{5+} cations, through adjustment of the molybdenum source power. Control over the concentration the Mo^{5+} valence state was achieved through decreases in the oxygen partial pressure facilitated via oxygen chemisorption by the molybdenum sputter flux at power levels of 0, 20, 40, 60, 80, and 100 W, while the Nb source was operated concurrently at a constant sputter power of 200 W. The resulting films, roughly 100 nm in thickness, were characterized using variable angle spectroscopic ellipsometry as well as x-ray photoelectron spectroscopy in order to derive a process-property relationship among molybdenum source power and its effects on the refractive index, extinction coefficient, optical band gap, as influenced by the relative concentrations of Mo^{5+} , Mo^{6+} , and Nb^{5+} cations. Increases in the molybdenum source power from 0 to 100 W allow for tailorability of the refractive index, $2.29 \leq n_{550} \leq 2.34$, extinction coefficient, $0.00 \leq k_{550} \leq 0.02$, and optical band gap, $3.05 \leq E_g \leq 3.48$ eV. The co-deposition procedure used within this work affords the ability to systematically adjust the content of the absorbing Mo^{5+} cations, from 0 to 3 at. %, within a dielectric matrix comprised of MoO_3 and Nb_2O_5 , presenting several opportunities in increasing the design-space for both optical coatings and electrochromic devices.

1. Introduction

Multi-component oxide thin films have found a large variety of uses in optics and electronics as a direct result of their ability to achieve properties unattainable in binary metal-oxide films. While the list of specific applications for multi-component oxides is vast, some noteworthy examples include transparent conductive materials [1-3] composed of indium-tin oxide and aluminum zinc oxide, rugate-type graded index filters [4,5], and switchable electrochromic smart-windows [6,7]. In addition to their electronic and optical applications, the deposition of multi-component oxide thin films has been associated with improved structural quality due to low surface roughness as well as lower deposition stresses [8-10]. While the ability to mix stoichiometric oxide species has provided a large number of options within the design-space for optical and electronic material development, several publications exploring multi-component oxide systems doped with substoichiometric oxides have highlighted methods for obtaining films with an even wider variety of optical and electronic properties. Specifically, recent works, including several detailed studies by Gil-Rostra et al. [11-16], have demonstrated the ability to systematically tailor the optical absorption of “ionic glass” thin films consisting of metal-cation doped dielectric thin films, by adjusting the dopant element, as well as its valence state and concentration. With respect to optical coatings, the aforementioned methods are of particular interest due to their ability to tailor not only the refractive index, but the extinction coefficient as well [12,17]. In particular, the capability to leverage the extinction coefficient provides several benefits for the development of ophthalmic coatings [11], plasmonic materials [18,19], light emitting diode components [20-22], and photovoltaics [1].

Typically, fabrication of optically absorbing mixed-oxide coatings requires a stable, dielectric oxide matrix that is doped with metal cations corresponding to substoichiometric

oxides. Studies by Gil-Rostra et al. have deposited thin films (~300 nm) of SiO₂ doped with various transition metal oxides including, Fe, Zr, Co, W, Mo, Cu, and Ni [11-16]. Gil-Rostra et al. have explored combinations of transition metal oxides, including mixtures of W and Si oxides by way of glancing angle deposition, for use in electrochromic layers with tunable optical transmission and absorption [14]. While the amount of potential material mixtures is truly vast, this work focuses on the deposition and characterization of films composed of niobium pentoxide and mixed valent molybdenum oxides, hereby referred to as Nb_xMo_yO_z. Justification for the selection of the Nb-Mo-O material system is multifaceted, as both oxide systems possess a variety of valuable properties. For instance, both Nb₂O₅ and MoO₃ are of particular interest concerning applications in optics due to their respectively high refractive index values of 2.34 [23-25] and 2.14 [26,27] at $\lambda=550$ nm and wide optical gaps, $E_{g,Nb_2O_5} \sim 3.6$ [24] and $E_{g,MoO_3} \sim 3.2$ eV [27], rendering both materials transparent throughout visible wavelengths ($450 \leq \lambda \leq 700$ nm). Additionally, studies by Schmitt et al. [28] and Usha et al. [29,30] reported excellent electrochromic properties for sol-gel based, and RF deposited Nb₂O₅:MoO₃ mixtures, respectively. Schmitt et al. reported a coloration efficiency of 21.5 cm²/C for Nb₂O₅ doped with 0.4% MoO₃ [28]. Later work performed by Usha et al. exploring the electrochromic properties of Nb₂O₅:MoO₃ thin films reported maximum coloration efficiencies of 51.94 cm²/C and 69.80 cm²/C with ratios of 90:10 and 95:5, respectively [29,30]. Furthermore, mixtures of stoichiometric Nb₂O₅ and MoO₃, deposited via RF sputtering, had been explored by Usha et al. due to their potential n-type conductivity as a result of lattice substitution of Mo⁶⁺ for Nb⁵⁺ [29,31]. The Mo⁶⁺ ion is a prime candidate for doping into an Nb⁵⁺ host matrix as a result of its slightly smaller ionic radius of 62 pm, compared to that 69 pm for Nb⁵⁺, allowing for a potential increase in electron mobility [28,29,32]. Nb₂O₅ is well suited as the matrix material within

mixed-valent thin films due to its high structural stability, high melting temperature $T_m=1500\text{ }^{\circ}\text{C}$, and highly negative enthalpy of formation $\Delta_f H^{\circ} = -1899.5\text{ kJ/mol}$ [33]. In contrast to the low enthalpy of formation and high thermal stability of Nb_2O_5 , MoO_3 is relatively unstable, decomposing at $740\text{ }^{\circ}\text{C}$ and having a low-magnitude enthalpy of formation $\Delta_f H^{\circ} = -745.1\text{ kJ/mol}$ [33]. The relatively small magnitude of the enthalpy of formation for MoO_3 results in a low driving force for compound formation, rendering it easily reducible to the optically absorbing cation Mo^{5+} , corresponding to the surface phase Mo_2O_5 [34-36]. The facile reduction of MoO_3 to Mo_2O_5 during reactive magnetron co-sputtering, associated with optical gap and extinction coefficient tailorability, has been reported previously by our research group [17,37].

This work utilizes reactive magnetron co-sputtering to deposit mixed-valent $\text{Nb}_x\text{Mo}_y\text{O}_z$ films through manipulation of the oxygen content by using the Mo deposition flux as both a getter and an essential component within the films. The amount of oxygen available for compound formation was decreased through systematic increases in the Mo source power from 0 to 100 W, concurrent with Nb deposition at 200 W. The relative instability of MoO_3 , coupled with decreased oxygen levels, leads to the formation of Mo^{5+} , the presence of which can be leveraged in order to dope the films with absorptive cations, allowing for precise variation of the dispersion and magnitude of both the refractive index and extinction coefficient. Reactive co-sputtering was chosen for this series of experiments as a result of its high deposition rates, potential for industrial scalability, and the ability to control the reactive and inert gas mixtures present during film growth. A hybrid co-sputtering approach was utilized, wherein the Nb source was powered using pulsed-DC magnetron sputtering and the Mo source was deposited concurrently using continuous DC power. Note that pulsed-DC sputtering was utilized in order to ensure process stability, and eliminate arcing attributed to the formation of highly dielectric

Nb_2O_5 , $\epsilon=41$ [38], on the surface of the Nb cathode. The utilization of the co-sputtering approach, in favor of alloy target deposition, allows for independent variation of the applied cathode power, the mode of power application, magnet configuration, and target-to-substrate distance [17,39,40]. As such, the dynamic variable space afforded by the co-sputtering can be leveraged to allow for precise tuning of both film composition and chemistry [17]. This work reports on a comprehensive analysis of the effects of processing conditions on the resulting chemistry and optical properties of mixed-valent $\text{Nb}_x\text{Mo}_y\text{O}_z$ thin films. The present study is expected to contribute towards a fundamental understanding of mixed-valent, multi-component oxides and can be applicable to a large class of such materials. In addition, the study offers a template for the deposition of thin films with systematically varied amounts of absorptive metal cations in order to provide tailorability of the optical absorption, refractive index, and optical band gap of $\text{Nb}_x\text{Mo}_y\text{O}_z$ thin films.

2. Experimental

2.1. Deposition

All films were deposited within a stainless steel high vacuum chamber, as described in detail elsewhere [39]. Two 50 mm molybdenum (99.95%) and niobium (99.95%) targets (K.J. Lesker) were used as the precursor materials for this experiment. All depositions were performed on fused quartz optical blanks (25 mm diameter, 1.65 mm thickness) placed atop p-type silicon (100) witness samples (50 mm). Prior to deposition the chamber was evacuated to a base pressure of approximately 1×10^{-6} Torr, or better. Upon achieving the required base pressure, 25 sccm of argon (99.999%) was introduced into the chamber through an Alicat mass flow controller. Note that the argon inlet was placed in the vicinity of the two sputter sources; each placed 13 cm from the substrate. The argon pressure (P_{Ar}) was set at 2.0 mTorr by adjusting the

conductance through a VAT automated gate valve, resulting in a pumping speed of approximately 160 (± 2) l/s. Upon achieving a stable P_{Ar} , the gate valve position was locked and 10 sccm of oxygen (99.995%) was introduced through a port in the vicinity of the substrate. Under the prescribed experimental conditions, the oxygen partial pressure (P_{O_2}) remained steady at 0.8 mTorr prior to plasma ignition, leading to a total pressure (P_{Tot}) of 2.8 (± 0.05) mTorr at the start of each deposition. Co-deposition of niobium and molybdenum oxides was achieved using both an Advanced Energy Pinnacle Plus pulsed DC power supply in conjunction with an Advanced Energy W 500 DC power supply, respectively. The pulsed DC power supply responsible for niobium oxide deposition was set to operate at a constant power of 200 W. To reduce arc events, a 4.5 μ s reverse bias pulse was applied to the molybdenum cathode repeating at a frequency of 30 kHz of, resulting in a duty cycle of 87%. The DC power settings for molybdenum deposition (W_{Mo}), were set at 0, 20, 40, 60, 80, and 100 W (Table 1).

2.2. *Characterization*

X-ray photoelectron spectroscopy (XPS) analysis was employed to measure the composition and chemistry of the compounds present in the deposited films. XPS survey and high energy resolution scans were obtained using a Physical Electronics 5700 equipped with a monochromatic Al K α (1486.6 eV) x-ray source. Compositional analysis was performed using survey scans at an analyzer pass energy of 187.85 eV in a binding energy range spanning 0-1400 eV, while an analyzer pass energy of 29.35 eV was used for high energy resolution measurements to examine the chemical valence states of the deposited species. In order to correct for charging, 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 mixed Gaussian-Lorentzian line shapes following Shirley background subtraction. XPS data

processing was performed using the CasaXPS 2.3.16 software package. Note that doublet peak spacing, peak area ratios, and peak full-width half-maxima were all constrained in an effort to increase fit accuracy.

The optical properties of the $\text{Nb}_x\text{Mo}_y\text{O}_z$ films were measured using a J.A. Woollam VASE spectroscopic ellipsometer and fit using the WVASE32 software package [41]. The VASE instrument was used in both transmission (T) and spectroscopic ellipsometry (SE) modes over a wavelength range of 255-1700 nm (0.72-4.86 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 [41]. 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 was 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 ($n(\lambda)$), the extinction coefficient ($k(\lambda)$), 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 section 3.2, 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 [41]. Fits with an MSE greater than 15 were rejected.

3. Results and discussion

3.1. Dependence of Film Composition and Chemistry on Molybdenum Source Power

XPS survey scans, as presented in Figure 1, were performed in order to evaluate the composition of the Nb-Mo-O films as a function of increasing W_{Mo} . Mo 3d, Nb 3d, C 1s and O 1s core level transitions were used to determine composition. The amount of molybdenum present in the films increases in a nearly linear fashion, from 0.9% at $W_{Mo}=20$ W, to 10% when $W_{Mo}=100$ W. The survey scans demonstrate that the molybdenum composition increases systematically as a function of increasing W_{Mo} from 0-100 W, as displayed numerically in Table 2. In addition to molybdenum, niobium, and oxygen, carbon is also present. The presence of carbon, ranging from approximately 17-25% of the surface composition, is attributed to adventitious carbon species formed as a result of environmental exposure during transportation of the samples from the deposition chamber to the XPS analysis chamber. Note that no sputtering was performed to remove the carbon in order to avoid altering the chemistry of the Mo and Nb oxides. Besides the presence of adventitious carbon on the sample surface, no other impurity elements were detected.

High energy resolution XPS spectra of the 3d core level transitions for Nb and Mo, shown in Figure 2 and Figure 3, respectively, were acquired and fit in order to provide insight into the effects of increases in W_{Mo} on the valence states of the co-deposited Nb and Mo oxide species. The oxidation state of the Nb 3d doublet, as shown in Figure 2, appears to be relatively insensitive to increases in W_{Mo} , as evinced by their ability to be fit with a single pair of Gaussian-Lorentzian line shapes (30% Lorentzian) spaced 2.74 eV apart. Furthermore, the binding energies of the Nb 3d_{5/2} peaks were found to vary slightly between 206.9 and 207.4 eV, within the range commonly reported for the Nb⁵⁺ valence state corresponding to Nb₂O₅ [42-44]. Note that there is a systematic increase in the Nb 3d_{5/2} binding energy corresponding to increases in Mo content, a likely result of the differences in electronic polarizability and nearest neighbor

interactions among Nb and Mo cations. In contrast to the stability of the Nb^{5+} state, the chemistry of the molybdenum species (Figure 3) displays significant sensitivity to increases in W_{Mo} and the associated decreases in oxygen partial pressure listed in Table 1. The Mo 3d doublet was fit in a similar method as described for the Nb 3d core level transition, albeit with a constrained peak spacing of 3.13 eV. Note that the high energy resolution data observed at $W_{\text{Mo}}=0$ W demonstrates overlap between the Mo 3d doublet and the loss structure attributed to the Nb 3d doublet. The Nb loss structure was fit and subsequently subtracted in subsequent peak fits to ensure accurate peak areas for the Mo 3d doublet fits. As shown in Figure 3, the Mo^{6+} species is observed within the range of 233.0 to 232.5 eV for $W_{\text{Mo}} > 0$ W, in agreement with reported values for MoO_3 [42,45]. The Mo^{6+} valence state persists as the only molybdenum valence state present until W_{Mo} values exceed 40 W, leading to the concurrent formation of both Mo^{5+} and Mo^{6+} . The formation of the Mo^{5+} valence state leads to the formation of a second doublet with a $3d_{5/2}$ binding energy of ranging from 231.5 to 231.9 eV of as a result of the lower ionic character associated with the reduced compound [45]. The onset of the formation of Mo^{5+} is related to the drop in Po_2 from 0.8 to 0.6 mTorr, induced by gettering, or chemisorption of oxygen, as a result of the enhanced metallic molybdenum flux due to increases in W_{Mo} . Increases in W_{Mo} are correlated with increases in current, related to a larger Ar^+ flux at the surface of the target [46], thus increasing the amounts of sputtered molybdenum. As such, levels of Po_2 are shown to be precisely controlled (Table 1), giving rise to a moderately reducing chamber atmosphere that facilitates the formation of the Mo^{5+} cation. The reduction of the Mo^{6+} state is related to the shift from the oxygen rich “poisoned” regime, wherein the target surfaces are coated with dielectric oxides, to the “transition” regime, associated with partial sputter target oxidation [46,47]. Thus,

the onset of transition regime sputtering at $W_{Mo} \geq 60$ W represents a critical inflection point in the behavior of the chemistry of the $Nb_xMo_yO_z$ thin films.

3.2 Measurement of Optical Constants, Optical Gap, Thickness, and Surface Roughness

As mentioned previously, determinations of the optical constants, E_g , thickness, and surface roughness were performed through simultaneous fitting of transmission data captured at 90° incidence as well as raw polarization data gathered at 50, 55, and 60°. Note that the use of simultaneous fitting of VASE and transmission data ensures accurate calculation of the optical path length and the onset of the absorption edge attributed to the optical gap. The aforementioned optical and physical properties of the $Nb_xMo_yO_z$ thin films were characterized using a model consisting of a general oscillator layer consisting of a Tauc-Lorentz [48] and a Lorentz [41] oscillator atop a 1.65 mm quartz glass substrate layer. The Tauc-Lorentz oscillator, widely used for the characterization of amorphous semiconductors, is especially useful as a result of its direct parameterization of E_g [48,49]. The Lorentz term was required to accurately fit the measured polarization and transmission data, due to the onset of an absorption tail at energies below E_g ; a result of impurities and structural disorder observed in the amorphous $Nb_xMo_yO_z$ thin films. Finally, the ellipsometry model used in this study employs a roughness layer consisting of a Bruggeman effective medium approximation assuming a 50% void fraction at the film surface. Overlay plots of the model calculation and the transmission data, as well as the measured Ψ and Δ data, are shown in Figure 5 and Figure 6. Note the high quality of the simultaneous fitting, as demonstrated by the MSE values between 4.1 and 11.6 (Table 4).

Measurement of the films' surface roughness, as listed in Table 4 alongside additional fit parameters, indicates a slight increase in roughness from 1.2 to 1.7 nm for $0 \leq W_{Mo} \leq 80$ W. A marked increase in roughness is observed for $W_{Mo}=100$ W, corresponding to a value of 2.3 nm.

The observed roughness values are consistent with values reported for both amorphous Nb₂O₅ [25,50] and Mo doped Nb₂O₅ [29,30,51]. The increase in roughness, alongside increases in W_{Mo} , can be correlated directly with decreases in P_{O_2} from 0.7 to 0.5 mTorr. Oxygen partial pressure scales inversely with particle size, resulting in lower roughness values and smaller crystallite sizes at higher oxygen pressures due to the interruption of local epitaxy attributed to surface oxidation during nucleation [52,53]. Note that the films analyzed in this study were amorphous, as measured using x-ray diffraction (data not shown). However, the lack of diffraction features merely indicates that the crystallite size, coupled with a high degree of disorder, is not sufficient to give rise to Bragg scattering. As such, it is possible that the films are not purely amorphous but are comprised of highly disordered nano-scale crystallites, as previously reported by Kaiser for room-temperature deposited oxide thin films [53].

In addition to surface roughness, the deposition rate also showed significant sensitivity to increases in W_{Mo} . As shown in Table 3, the reported thickness values are near the thickness goal of 100 nm. The resulting rates vary from 8.1 to 28.5 nm/min corresponding to the increase in W_{Mo} from 0 to 100 W. The augmentation of the deposition rate, as a function of W_{Mo} , is the result of the contributions of the Mo sputter flux to the growing film. The effects of the increased levels of sputtered Mo are two fold, first being the deposition of increasing amounts of Mo adatoms, and second, the reduction in P_{O_2} attributed to oxygen gettering related to the chemisorption of gaseous oxygen via compound formation. The decreases in P_{O_2} , related to the transition from the poisoned to the transition sputtering mode, are related to the non-linear increases in the deposition rate occurring at $W_{Mo} > 40$ W. Note that the deposition rate scales in a nearly linear fashion with deposition current, as shown in Table 1. Increases in current, and

deposition rate, are directly related to increases in sputter yield, brought on by the depletion of surface oxides on the sputter targets [46].

The spectral response of the optical constants, $n(\lambda)$ and $k(\lambda)$, are depicted in Figure 7 and Figure 8. For $W_{Mo} < 100$ W, both $n(\lambda)$ and $k(\lambda)$ demonstrate behaviors analogous to dielectric, wide band gap semiconductors, with $k(\lambda) < 0.01$ for $\lambda > 400$ nm. For $W_{Mo} = 100$ W, a marked increase in k , where $k_{550} = 0.02$, is noted as a result of energy loss via electron-impurity and electron-electron interaction related to the presence of oxygen vacancies associated with the presence of 3% of the Mo^{5+} cation, as measured via XPS (Figure 3, Figure 4) [30,54]. Note that both n and k demonstrate a large increase in magnitude at wavelengths approaching the optical band gap. The response of $k(\lambda)$, as a function of W_{Mo} indicates a systematic red shift with increasing W_{Mo} . For all values of W_{Mo} , a significant tail is present at energies below the band edge. The presence of the observed absorption tail has been previously reported for amorphous and crystalline Nb_2O_5 as a result of scattering losses attributed to surface roughness and defect structure present within the films [29,50,51,55]. In addition to the effects of W_{Mo} on $k(\lambda)$, the magnitude of n_{550} can be tailored between 2.35 and 2.29, as a function of increasing W_{Mo} up until $W_{Mo} = 100$ W, where n increases slightly as a potential result of an increase in electronic polarizability or density attributed to the formation of significant quantities of the Mo^{5+} cation [56]. The gradual decreases in $n(\lambda)$ with increasing W_{Mo} from 0-80 W correspond to the increased MoO_3 content within the films, due to the lower refractive index of MoO_3 $n_{550} = 2.14$ [26] compared to that of Nb_2O_5 , observed for films deposited at $W_{Mo} = 0$ W, where $n_{550} = 2.34$. While MoO_3 is slightly more dense than Nb_2O_5 , with densities of 4.69 and 4.47 g/cm³, respectively, the electronic polarizability of the Nb^{5+} cation is 0.242 Å³ versus 0.169 Å³ for Mo^{6+} [57]. Given that the electronic polarizability is analogous to how tightly the electrons are held to

the nucleus via coulombic attraction, larger electronic polarizability values are related to increased electron shell density, resulting in an increase in the refractive index [57]. Note that n is slightly higher for $W_{Mo}=20$ W than for $W_{Mo}=0$ W. Again this minor increase in refractive index ($\Delta n_{550}=0.01$) could be the result of changes in the electronic polarizability as a result of nearest neighbor interactions. The gradual decrease in n_{550} observed for W_{Mo} values increasing from 20 to 80 W, is in agreement with increase in Mo^{6+} content measured via XPS (Figure 4). The ratio of $MoO_3:Nb_2O_5$ increases from 0.05 to 0.92. Using a rule of mixtures approximation, neglecting contributions from Mo^{5+} , the expected n_{550} value for this composite film is roughly 2.24, close to the observed value of 2.29.

3.3 *Impact of Molybdenum Valence State and Concentration on Band Structure*

As mentioned in the previous section, the spectral dispersion behavior of n and k demonstrates significant sensitivity to molybdenum content and chemistry. One of the most significant factors governing the spectral response of the optical constants is the onset of fundamental absorption related to the optical band gap of the $Nb_xMo_yO_z$ thin films. As evinced by the rapid decrease in transmission in Figure 5 as well as the large increase in k shown in Figure 8, the processing conditions, namely W_{Mo} and P_{O_2} , can be systematically adjusted to vary the optical properties of the deposited thin films. Increases in W_{Mo} , as discussed previously, result in the deposition of increasing amounts of Mo^{6+} , as well as Mo^{5+} species when $W_{Mo} \geq 60$ W. As shown in Figure 9, the optical gap values steadily decrease from 3.48 eV at $W_{Mo}=0$ W to 3.05 eV at $W_{Mo}=100$ W, alongside increases in $MoO_3:Nb_2O_5$ from 0 to 0.86. The linear decrease in E_g as a function of increasing MoO_3 content is a result of the lower E_g of MoO_3 , typically ranging between 2.7 to 3.2 eV, depending on processing conditions [6,27,37,56,58], compared to E_g ranges of 3.3 to 3.6 eV for Nb_2O_5 [24,25,30,51,59]. As W_{Mo} increases from 60 to 100 W, leading to

higher concentrations of both Mo^{6+} and Mo^{5+} , the drop in E_g , while still linear, occurs more rapidly. The rapid drop in E_g observed for $W_{\text{Mo}} \geq 60$ W is directly correlated to the presence of Mo^{5+} , occurring at concentrations of 1.0, 1.5, and 3.0% for W_{Mo} values of 60, 80, and 100, respectively. Decreases in E_g as a result of increasing concentration of both Mo^{6+} and Mo^{5+} are related to the formation of Mo 4d impurity levels at energies beneath the Nb 4d band. The presence of Mo^{5+} results in the formation of additional impurity levels within the previously unfilled lower portion of the Mo 4d t_{2g} and O 2p bands, resulting in a net shrinkage of E_g [6,35]. The rapid decreases in E_g at $W_{\text{Mo}} \geq 60$ can be directly correlated to the onset of the transition mode of sputtering.

4. Conclusions

This work reports a comprehensive exploration of the changes in both the optical and chemical properties of mixed-valent thin films comprised of $\text{Nb}_x\text{Mo}_y\text{O}_z$, as a function of molybdenum oxide content and chemistry. The molybdenum content and chemistry could be controlled through adjustments in the power applied to the molybdenum sputter source, resulting in tailorability of the optical constants, n and k , as well as E_g . Increases in W_{Mo} from 0 to 40 W yield dielectric mixtures of MoO_3 and Nb_2O_5 , related to E_g values decreasing linearly from 3.48 to 3.38 eV as a function of increasing MoO_3 content. The dielectric nature of the co-deposited MoO_3 (Mo^{6+}) and Nb_2O_5 (Nb^{5+}) for $0 \leq W_{\text{Mo}} \leq 40$ is analogous to poisoned mode sputtering, as evinced by the low deposition rates and stoichiometry of the resulting compounds. Further increases in W_{Mo} , from 60 to 100 W, related to transition mode sputtering, led to the formation the Mo^{5+} species. The chemistry of the molybdenum oxide species within these films could be controlled as a function of W_{Mo} , resulting in the incorporation of 1 to 3 atomic percent of Mo^{5+} within a transparent matrix of MoO_3 and Nb_2O_5 . As such, the co-deposition method reported

here allows for the systematic variation of the concentration of absorbing Mo^{5+} cations, while achieving precise control over the spectral response of n and k as well as the magnitude of E_g . The ability to precisely tailor the refractive index, $2.34 \leq n_{550} \leq 2.29$, and the extinction coefficient, $0.00 \leq k_{550} \leq 0.02$, is especially important for the deposition of high index, transparent layers within multilayer interference filters. Additionally, the systematic variation of E_g from 3.48 to 3.05 eV encompasses a useful spectral range for devices operating throughout UV and visible wavelengths. Finally, the co-deposition procedure used here affords the ability to systematically adjust the content of the absorbing metal-oxide cations within a dielectric matrix, presenting several opportunities in increasing the design-space for both optical coatings and electrochromic devices.

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Figure Captions

Figure 1. Survey spectra used for analysis of composition for MoO_x reference samples (100 W Mo, 0 W Nb), mixed component Nb₂O₅:MoO_x (200 W Nb, 100 W Mo), and Nb₂O₅ (200 W Nb, 0 W Mo). Spectra are offset for clarity. To improve readability, only highly intense peaks are labeled.

Figure 2. High energy resolution scans of Nb 3d transitions for varying levels of molybdenum deposition power. Spectra are offset for clarity.

Figure 3. High energy resolution scans of Mo 3d transitions for varying levels of molybdenum source power (W_{Mo}). Note that the Nb loss structure was fit in addition to the Mo core level spectra in order to reduce error in peak area measurement. Spectra are offset for clarity.

Figure 4. Stacked column graph of relative amounts of niobium and molybdenum compounds as a function of molybdenum source power (W_{Mo}).

Figure 5. Transmission spectra, and associated model fits (dotted lines) measured using a J.A. Woollam spectroscopic ellipsometer in transmission mode.

Figure 6. Plot of ellipsometry parameters Ψ and Δ , as well as associated model fits (dashed lines) for angles of 50°, 55°, and 60°.

Figure 7. Plot of refractive index for films with increasing Mo content.

Figure 8. Plot of extinction coefficient for increasing Mo content.

Figure 9. Plot of optical band gap as a function of molybdenum source power, W_{Mo} .

Table 1. Deposition parameters used for the fabrication of Nb_xMo_yO_z mixed oxide thin films

Molybdenum-Continuous DC			Niobium-Pulsed DC			P _{O2} (mTorr)
Power (W)	Voltage (V)	Current (A)	Power (W)	Voltage (V)	Current (A)	
0	11	0	200	526	0.38	0.7
20	446	0.04	200	616	0.36	0.7
40	483	0.08	200	606	0.33	0.8
60	515	0.11	200	619	0.32	0.6
80	545	0.14	200	595	0.34	0.6
100	560	0.17	200	605	0.33	0.5

Table 2. Nb_xMo_yO_z thin film compositions obtained from XPS survey spectra

W _{Mo} (W)	Transition	Binding Energy (eV)	Composition (at%)
0	C 1s	284.6	17.3
	O 1s	530.2	59.0
	Nb 3d	207.0	23.6
20	C 1s	284.7	16.7
	O 1s	530.3	59.2
	Nb 3d	207.1	22.9
	Mo 3d	232.7	1.2
40	C 1s	284.7	19.0
	O 1s	530.3	58.1
	Nb 3d	207.1	19.3
	Mo 3d	232.7	3.5
60	C 1s	284.9	18.6
	O 1s	530.5	59.0
	Nb 3d	207.3	16.9
	Mo 3d	232.9	5.6
80	C 1s	284.4	20.2
	O 1s	530.8	57.8
	Nb 3d	207.6	13.5
	Mo 3d	232.4	8.5
100	C 1s	285.5	20.7
	O 1s	531.9	57.0
	Nb 3d	207.9	11.7
	Mo 3d	233.5	10.6
MoO _x Ref.	C 1s	287.9	24.6
	O 1s	534.3	54.6
	Nb 3d	195.9	0.0
	Mo 3d	235.9	20.8

Table 3. Optical constants, optical gap, surface roughness, thickness and deposition rate data obtained from spectroscopic ellipsometry and transmission measurements.

W_{Mo} (W)	n_{550}	k_{550}	E_g (eV)	Roughness (nm)	Thickness (nm)	Deposition rate (nm/min)
0	2.34	0.00	3.48	1.2	99.0	8.1
20	2.35	0.00	3.44	1.4	105.0	13.8
40	2.33	0.00	3.38	1.4	104.1	17.3
60	2.31	0.00	3.34	1.5	104.9	17.8
80	2.29	0.00	3.22	1.7	109.2	26.1
100	2.29	0.02	3.05	2.3	108.6	28.5

Table 4. Numerical values for fit parameters used in the calculation of optical constants, thickness, and roughness for niobium oxide films with varying levels of molybdenum oxides and suboxides. Note that these values represent raw data exported directly from the J.A. Woollam W-VASE 32 software package. Reflectance of the back surface is parameterized using the term BackRefl. Additional parameters, Amp, En, and Eg, represent oscillator amplitude, centroid, and band gap (Tauc-Lorentz only).

Parameter	W _{Mo} (W)					
	0	20	40	60	80	100
MSE	5.218	4.419	4.144	4.592	4.826	11.64
BackRefl	0.83341±0.00187	0.87264±0.00223	0.77097±0.00142	0.4579±0.00138	0.70372±0.00153	0.6221±0.00455
Amp1	505.69±5.44	508.6±5.04	509.85±2.85	482.66±2.98	422.47±2.56	110.68±44.1
En1	3.9997±0.0228	3.9656±0.0231	3.6341±0.0109	3.6063±0.0079	3.53±0.0155	3.2135±0.0294
Eg1	3.4776±0.00199	3.4378±0.00185	3.3768±0.00101	3.3431±0.00106	3.2213±0.00119	3.2303±1.92e+009*
Roughness (nm)	1.214±0.0175	1.415±0.0228	1.379±0.0138	1.529±0.0148	1.676±0.016	2.349±0.0391
Amp2	2.7992±0.0358	2.64±0.0379	2.1169±0.0239	1.8638±0.0254	1.8034±0.0244	0.49121±1.47
En2	4.3562±0.00216	4.3425±0.00213	4.3489±0.00198	4.352±0.00279	4.3404±0.00272	7.4126±5.01
Br2	0.34553±0.00283	0.31171±0.00333	0.33088±0.00284	0.39527±0.00344	0.35417±0.00397	5.6546±2.75
Thickness (nm)	99.013±0.0132	105.040±0.016	104.081±0.0106	104.895±0.0119	109.185±0.0124	108.581±0.0308
Amp3	-	-	-	-	-	67.65±16
En3	-	-	-	-	-	4.5715±0.0479
Eg3	-	-	-	-	-	3.0563±0.0201

*Superfluous parameter, not included in optical property calculations

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9