Physical Characterization of Sputter-Deposited Amorphous Tungsten Oxynitride Thin Films

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ABSTRACT

Tungsten oxynitride (W-O-N) thin films were deposited onto silicon (100) and quartz substrates using direct current (DC) sputtering. Composition variations in the W-O-N films were obtained by varying the nitrogen gas flow rate from 0 to 20 sccm, while keeping the total gas flow constant at 40 sccm using 20 sccm of argon with the balance comprised of oxygen. The resulting crystallinity, optical properties, and chemical composition of the DC sputtered W-O-N films were evaluated. **All the W-O-N films measured were shown to be amorphous using x-ray diffraction. Spectrophotometry results indicate that the optical parameters**, namely, the transmission magnitude and band gap (E_g), are highly dependent on the nitrogen content in the reactive gas mixture. Within the W-O-N system, E_g was able to be precisely tailored between 2.9 eV and 1.9 eV, corresponding to fully stoichiometric WO_3 and highly nitrided W-O-N, respectively. **Rutherford backscattering spectrometry (RBS) coupled with X-ray photoelectron spectroscopy (XPS)** measurements indicate that the composition of the films varies from WO_3 to W-O-N composite oxynitride films.

Keywords: Tungsten oxynitride; Sputtering; Band gap; Composition

1. Introduction

Tungsten oxide (WO_3) is a widely studied “chromogenic” material with interesting structural, electronic, and optical properties for utilization in many scientific and technological applications [1-10]. Among metal oxide semiconductors, WO_3 has become a focal point of interest where nanostructured and low-dimensional forms of WO_3 are beneficial for technological development. WO_3 thin films and nanostructures exhibit an optical band gap ($\sim 2.4\text{-}3.2$ eV, depending on processing conditions) that permits efficient use of the solar spectrum including absorption in the blue part of the visible region and the ultraviolet region, as well as a high transmission region that extends from the near-infrared (IR) to the visible spectrum [1-4]. Coupled with good electronic transport properties, photosensitivity, and chemical integrity, WO_3 -based materials are attractive for applications related to sustainable energy production including energy efficient windows and architecture, photoelectrochemical water-splitting, photocatalysis, and solar cells [1-9].

WO_3 is a complex material, with respect to crystal structure and thermal stability, as a result of the high degree of polymorphism exhibited by both stoichiometric and non-stoichiometric W oxides [11-13]. **The phase transitions of WO_3 are based on a distorted ReO_3 structure. The specific phase existence are the phase transitions** are predominantly temperature dependent following a sequence of low temperature monoclinic structure, $\epsilon\text{-WO}_3$ below 230 °K, triclinic, $\delta\text{-WO}_3$ from 230-300 °K, room temperature monoclinic, $\gamma\text{-WO}_3$ from 300-600 °K, orthorhombic, $\beta\text{-WO}_3$ from 600-1020 °K, and a tetragonal structure, $\alpha_1\text{-WO}_3$ above 1170 °K [11-13]. The optical properties and lattice structure associated with WO_3 allow feasible field-aided ion intercalation which is needed to accommodate the change in oxidation state and

promote reversible spectral absorption properties [14-17]. **Both stoichiometric and non-stoichiometric W-oxide based materials are, therefore, quite important and offer a platform to further investigate the fundamental structure-property relationships for utilization in optical and electronic device applications.**

Currently, significant attention is directed towards multifunctional thin films and coatings that combine the mechanical properties of transition metal nitrides with the electro-optical properties of their counterpart metal oxides. The **oxynitride** family of materials, which can be represented chemically by MO_xN_y , or M-O-N , can offer advantages over the nitride-oxide end members, providing the ability to tune the desired properties based on the chemical composition. In addition, oxynitrides can also combine the traditional advantages of nitrides, such as oxidation resistance and structural stability at elevated temperatures. The focus of the present work is the synthesis and physical characterization of tungsten oxynitride films. **Tungsten nitrides have been widely studied for their use as diffusion barriers in microelectronics** [18-20], gate electrodes in semiconductor devices [21,22], hard coatings to protect from mechanical wear [23-25], or as Schottky contacts [27]. Several of the early studies have contributed extensively towards the understanding of W-N system, especially the knowledge of fundamental relationship between different parameters, such as deposition conditions and their effect on the internal stress, microstructure, and elemental concentration [18-31]. Similarly, tungsten oxides have been studied for a wide variety of electrical, optical, and energy related applications [1-12]. However, compared to work reported on Ti-based oxynitrides, studies focused on W-oxynitrides are meager. Mohamed et al. have studied W-oxynitride films with a low concentration of nitrogen incorporation for the purpose of tuning structural, optical, and electrical properties for temperature dependent resistors, diffusion barriers, and gate **materials** [10]. These authors have

later expanded the investigations to the composition of tungsten oxynitrides to include higher concentrations of nitrogen, resulting in a higher index of refraction in nitrogen doped tungsten oxide films [32]. Chawla et al. conducted a study with the goal of extending light harvesting capability of the films to a wider portion of the solar spectrum and found that nitrogen doping of tungsten oxide does in fact lower the band gap [8]. Vemuri et al. attempted to manufacture rf-sputtered low resistive nitrogen doped tungsten oxide films, with fundamental absorption shifted to longer wavelengths, and concluded that the conductivity of said films is lowered with increased nitrogen content [33]. **While earlier efforts were focused on either thicker coatings (several microns) or a specific phase, where complications arise when nitrogen induced amorphization leads to reduced thickness or structural effects, the present work is focused towards understanding the effect of nitrogen content in reactive sputter-deposition of amorphous W-O-N films for a set of samples with controlled film thickness of 100 nm. The results obtained are presented and discussed in this paper.**

2. Experimental

2.1 Fabrication

Thin films of W-O-N were deposited onto clean silicon (Si) (100) and optical grade quartz substrates by direct current (DC) sputtering. Silicon substrates were cleaned by RCA (Radio Corporation of America) cleaning. Quartz substrates were cleaned with isopropanol. All the substrates were dried before introducing into the vacuum chamber, which had been evacuated to a base pressure of $\sim 3 \times 10^{-7}$ Torr. Tungsten (W) metal target (Plasmaterials Inc.) of 2" diameter and 99.95% purity was employed for reactive sputtering. DC power was supplied to the W-target by an Advanced Energy MDX 500 DC power supply with the sputtering gun at a distance of 80 mm from the substrates. **Once an adequate base pressure was reached, 20**

sccm of argon was flowed into the chamber and 100 Watts of power was supplied to ignite the plasma. For reactive **deposition of** W-O-N films, oxygen and nitrogen were employed along with argon. The total gas flow was kept constant at 40 sccm, resulting in a working pressure of 10 mTorr at a pumping speed of 50 L/s. The argon flow rate was held constant at 20 sccm while the values of total oxygen and nitrogen gas flow were adjusted to a total of 20 sccm. The ratio of nitrogen to oxygen was varied in order to understand the effects of nitrogen content on the physical and optical properties of W-O-N films. The processing conditions are summarized in Table 1. Before each deposition, the target was pre-sputtered for 10 minutes using Ar with the gun shutter closed. The depositions were carried out at room temperature (25 °C). Deposition was made for a time period to reach a film thickness of ≈ 100 nm, as measured by in situ ellipsometry.

2.2 Characterization

The W-O-N films were characterized using various analytical techniques to understand their structural, **chemical, and optical properties**. X-ray diffraction (XRD) measurements on the samples grown on Si(100) were performed by using a Bruker D8 Advance x-ray diffractometer. In order to avoid unwanted substrate interaction, grazing incidence X-ray diffraction (GIXRD) measurements were performed on the films. All of the measurements were performed **ex situ** as a function of nitrogen fraction. GIXRD patterns were recorded using Cu K α radiation ($\lambda=1.54056$ Å) at room temperature. A voltage of 40 kV was used to generate the X-rays. GIXRD patterns were recorded employing the X-ray beam fixed at a grazing incidence of 1°. The scanning was performed in a 2θ range of 15-70° using the “detector scan” mode, where the detector was independently moved in the plane of incidence to collect the diffraction pattern. The step size and the scan speed were 0.05° (2θ) and 5°/min, respectively. **The nitrogen uptake**

and composition of the W-O-N films has been determined using an X-ray photoelectron spectroscopy (XPS) system (Staib Instruments Inc.). The instrument consists of an X-ray tube with Mg and Al sources (model RQ 300) and an integrated 5 keV electron gun (for Auger excitation) for XPS/Auger spectroscopy (model DESA 100). An Al anode (Al K α X-ray source; 1486.6 eV) was used for all the experiments. Survey scans were obtained using a 200 ms dwell time with 0.5 eV step. High energy resolution scans were performed using a step interval of 0.125 eV and a dwell time of 10 ms/step. To fit the high energy resolution spectra, Gaussian-Lorentzian line shapes were used along with Shirley background subtraction for accurate peak area determination. Rutherford backscattering spectrometry (RBS) measurements were also performed on the W-O-N samples to further understand the chemical composition and elemental depth distribution. An incident ion probe containing 1.5 MeV $^4\text{He}^+$ with a normal incident to the sample was used. The backscattered ions were detected using a silicon barrier detector at a scattering angle of 150°. Composition profiles were determined by comparing SIMNRA computer simulations [34,35] of the spectra with the experimental data.

Transmission measurements, performed using a Cary 5000 UV-VIS-NIR double-beam spectrophotometer, were obtained in order to investigate the transmission magnitude and band gap of the W-O-N films. W-N-O films grown on optical grade quartz were employed for these measurements. The quartz substrates extend the transparency range down to ~190 nm (6.5 eV), which is more than sufficient to determine the band gap (E_g) shift in deficient or stoichiometric or metal incorporated WO₃ films, as well as the N-doped tungsten oxide films. Optical constants, namely refractive index (n) and extinction coefficient values (k), were measured using spectroscopic ellipsometry. A J.A. Woollam

alpha-SE ellipsometer was used to measure the magnitude (Ψ) phase difference (Δ) of polarized light, at angles of 65°, 70°, and 75°, after interaction with the W-O-N film layer and substrate. Values for E_g and k were obtained by fitting the raw polarization data with a Tauc-Lorentz oscillator (TL), similar to models used to previously characterize WO_3 or Ti-doped WO_3 amorphous films [2,36]. The model's mean squared error (MSE) was then minimized using the Levenberg-Marquardt algorithm [37-39]. The Tauc-Lorentz model was used for this study due to its ability to directly calculate E_g for amorphous semiconducting materials [2,40].

3. Results

Grazing incidence X-ray diffraction (GIXRD) patterns of the **W-O-N films** are shown in Figure 1 **as a function of nitrogen flow rate**. It is evident that the patterns are diffuse without presence of any peaks which is an **indication** of amorphous film formation for all conditions used.

The optical transmittance spectra of W-O-N films are shown in Figure 2. The spectral transmission curves reveal that the W-O-N films, in general, show a high transparency in the measured spectral **region (250-800 nm)**, except where the incident radiation is absorbed across the band gap (E_g). This observation indicates the high-quality and transparent nature of **the deposited W-O-N films**. **It is evident that the spectral transmission curves undergo incremental changes as a result of increasing the nitrogen content**. Most notable is the **red-shift** in spectral absorption coupled with **decreased spectral transmittance** for W-O-N films, indicating a significant change in the electronic structure of the W-O-N films as a function of nitrogen content. **Therefore, further analysis of band gap (E_g , related to electronic structure)**

and extinction coefficient (k , related to optical quality and transparent nature) of the W-O-N films has been performed using the ellipsometry functions and TL-model fitting.

The Tauc–Lorentz (TL) model approach for empirical parameterization is based on the Tauc expression for the imaginary part (ϵ_2) of the dielectric function [36-39]. For a single transition, the complex dielectric function ϵ_2 is defined as [37-39]:

$$\epsilon_2(E) = \left[\frac{AE_0 C (E - E_g)^2}{(E^2 - E_0^2)^2 + C^2 E^2} \cdot \frac{1}{E} \right] \quad [1]$$

where E_0 is the resonance energy, E_g represents band gap energy, E photon energy, and A , C are the amplitude and broadening coefficient of ϵ_2 peak, respectively. The aforementioned model allowed for the determination of the optical parameters as well as thickness verification. Note that the real and imaginary parts of the dielectric function are related to the n and k as: $\epsilon_1 = n^2 - k^2$; $\epsilon_2 = 2nk$. Furthermore, this particular TL model has been proven effective, in the literature, to account for the optical properties of transparent oxides [2,36,40-42]. Therefore, the W-O-N films were modeled with TL-oscillator while attempting to locate the best fit for the data by minimizing the MSE. The modeling parameters of the W-O-N films deposited under variable nitrogen gas flow rate are listed in Table 2. The TL oscillator has 4 unique parameters associated with it and they are the amplitude (A) of the ϵ_2 peak, the half width (C) of the ϵ_2 peak, fixed center energy (E_0) of the TL peak, and the Tauc gap (E_g). The changes in electronic structure as a result of nitrogen incorporation are, thus, expected to reflect changes in E_g and k values. The variation of E_g values, as a function of with nitrogen flow rate is presented in Figure 3. The estimated uncertainty is $\pm 3\%$. The E_g for W-O-N films grown without any nitrogen is ~ 2.99

eV, which agrees well with those reported for pure WO₃ films [1-10]. It can be noted that the E_g values were not affected until a certain nitrogen flow rate is reached and then experience a progressive decrease with increasing nitrogen content. The trend observed (Fig. 3) with nitrogen flow rate can be attributed to both oxide and nitride behavior having an influence on the band gap of the samples indicating a **composite-like** material. As noted by Mohamed et al., there is a transition from insulating WO₃ towards metallic W₂N, which is reflected in the significant E_g decrease as nitrogen flow increases, as seen in Figure 3 [10,32]. Similar E_g behavior has been reported for tantalum oxynitride [43] and titanium oxynitride [44], where a transition from the behavior of an oxide to that of a nitride was attributed as the primary reason. Tantalum oxynitride acts as a composite material and as nitrogen or oxygen is substituted into the lattice it causes a change in the optical properties of the film [45]. Therefore, based on the observed optical absorption curves, we believe that the W-O-N thin films exhibit a **composite structure alongside** semiconducting behavior. Further evidence of effective nitrogen incorporation, after a nitrogen flow rate of 9 sccm, is derived from chemical composition analyses of the W-O-N films.

The most important optical parameters determined from SE data are the optical constants namely the index of refraction (n) and extinction coefficient (k). The variation in optical constants of W-O-N films at 550 and 623 nm are shown in Figure 4. It is evident that ' k ' values are low and very close to zero in most part of the spectrum (Fig. 4) which indicates very low optical losses due to absorption i.e., high optical transparency of the films. However, k values slightly increase with increasing nitrogen flow. The n values for W-O-N films exhibit a clear trend with nitrogen flow rate. The increase ' n ' values with increasing nitrogen flow rate is attributed to the insulating-to-semiconducting and then to semi-metallic type W-O-N films with

increase in nitrogen content in the films. The n values obtained for films grown without nitrogen corresponds to WO_3 and agree well with the literature values for pure WO_3 [2,36].

Chemical analyses using XPS and RBS were utilized in order to understand the observed electronic and optical property changes in W-O-N films as a function of nitrogen content. The XPS survey spectra were utilized to identify the elements present in W-O-N films deposited as a function of variable nitrogen gas flow rate. The typical XPS survey spectrum of a W-O-N film deposited at a nitrogen flow rate of 9 sccm is shown in Figure 5. The XPS data are shown in the binding energy (BE) range of 0-600 eV. All the spectral features, except the C 1s level, are attributed to the constituent elements present in the samples. XPS survey spectra of all the W-O-N films indicate that W, O and N were the main constituent elements of the samples except the C present in the sample surface. The W 4f, O 1s and N 1s peaks and their respective BE positions are as indicated in Figure 5. The C 1s signal is due to hydrocarbons adsorbed on the film surface during air exposure during transfer from the growth chamber to the XPS instrument. The absence of a Si substrate peak is due to the fact that the deposited W-O-N films cover the Si surface and are sufficiently thick to prevent detection of photoelectrons from the substrate.

The primary focus and purpose of XPS analysis was to understand the nitrogen uptake during deposition to form W-O-N compound. For the purpose, the N 1s core level peak was recorded and analyzed further. The N 1s peak stack plot as function of nitrogen gas flow rate is presented in Figure 6. It can be seen that the N 1s peak intensity increases with increasing nitrogen flow rate (Fig. 6a). The N 1s peak area has been determined after the peak fitting procedure outlined under Experimental section. The N 1s peak area evolution as a function of nitrogen flow rate is shown in Figure 6b. It can be seen that the

peak area increases dramatically for nitrogen flow rates of 9 sccm and above. Thus, the increases in the N 1s peak area, analogous to higher nitrogen content, correlate directly with a decrease in both spectral transmission and E_g .

Quantification of the elemental composition was made primarily from RBS measurements. Experimental RBS spectra, and associated simulations, of W-O-N films are shown in Figure 7. The backscattered ions observed were due to various elements and their respective energy positions, as indicated with arrows for the experimental spectra. The scattering attributed to W, the heaviest among the elements present in either the film or substrate, occurs at higher backscattered energy. Similarly, peaks attributed to backscattering events from Si, O, and N are as shown in the RBS spectra of W-O-N films (Figure 7). The measured height and width of the respective peaks are related to the concentration and thickness distribution of W, O and N atoms in the oxynitride film. Peak areas serve as a calibration check for composition and thickness since known Rutherford scattering cross section and experimental parameters can be used to calculate this height and width. The composition of the films were determined by simulating the experimental spectrum for the set of experimental conditions. The experimental curve (circles) along with the simulation curve (lines) calculated using SIMNRA code is as shown in Figure 7. The simulated curve was calculated using SIMNRA code [34] for the fixed set of experimental parameters: (1) incident He^+ ion energy, (2) integrated charge, (3) energy resolution of the detector, and (4) scattering geometry. It can be seen in Figure 6 that the simulated curves (solid line) calculated using the experimental parameters are in good agreement with the experimental RBS spectra. This observation indicates that film composition reasonably simulates the spectra and, hence, provides the estimate of film

composition. The W-O-N films grown without any nitrogen corresponds to stoichiometric WO_3 (W:25% and O:75%). Corroborating with XPS analyses, RBS measurements also indicate that the nitrogen incorporation is not very effective for the set of nitrogen flow rates ≤ 9 sccm, at which point an increase in the nitrogen concentration is noted confirming the formation of W-O-N films. Incorporation of nitrogen content in the films accompanied by a decrease in oxygen content. The estimated composition, at 9 sccm of nitrogen, from RBS data is $\text{WO}_{2.60}\text{N}_{0.40}$. Further increases in nitrogen content, and decreases in oxygen, are noted in the W-O-N films for nitrogen flow rates ≥ 9 sccm. The variation of nitrogen and oxygen content as a function of nitrogen flow rate is shown in Figure 7. RBS data confirms that the composition of the W-O-N films progress through the sequence $\text{WO}_3 \rightarrow \text{WO}_{2.60}\text{N}_{0.40} \rightarrow \text{WO}_{2.48}\text{N}_{0.52} \rightarrow \text{WO}_{2.20}\text{N}_{0.80}$.

4. Discussion

All the W-O-N films deposited are amorphous regardless the nitrogen flow rate employed. The amorphous structure of the W-O-N films (Figure 1) is attributed to the absence of additional energy during deposition. In general, in the sputter-deposition process, the additional energy for film growth is supplied by the substrate heating or substrate bias voltage. However, in the present case, neither substrate heating nor substrate bias voltage is maintained during W-O-N film deposition. Therefore, in the absence of additional thermal or electrical energy, the period of the atomic jump process of adatoms on the substrate surface is very large, the condensed species may stay stuck to the regions where they are landing thus leading to an amorphous films as noted earlier for several of W-oxide or W-Ti mixed oxide thin films [2,9].

The most interesting and remarkable feature of the work is the band gap decrease with increasing nitrogen flow rate. As can be seen in Figure 3, there is a decrease in optical band gap **value as the nitrogen flow** is increased. The more or less constant value of E_g for W-O-N up to a critical value of 9 sccm of nitrogen is due to the fact that the incorporation of nitrogen into W-oxide **matrix** is not effective at lower flow rates of nitrogen. However, after the critical nitrogen flow rate of 9 sccm, E_g decreases significantly which is a direct consequence of effective nitrogen incorporation and formation of W-O-N films. **XPS data confirmed the increasing nitrogen content in the films which is significant for nitrogen flow rates starting from 9 sccm and higher. Quantitative analysis using RBS data confirm that the W-O-N film formation follows the sequence of $WO_3 \rightarrow WO_{2.60}N_{0.40} \rightarrow WO_{2.48}N_{0.52} \rightarrow WO_{2.20}N_{0.80}$ with increasing nitrogen flow rate during deposition. Thus, the observed band gap shift and optical changes must be a direct consequence of nitrogen incorporation into W-oxide.** While the exact amount of nitrogen incorporation and E_g values are not readily comparable since both depend on processing conditions and method of preparation, the decreasing trend in E_g has been reported before by several authors, explaining that band gap values falls when there are increased amounts of nitrogen incorporation [5, 8, 10]. The physics behind the observed phenomenon can be explained based on two different approaches. Change in ionicity due to the incorporation of nitrogen atoms into oxide lattice causing E_g decrease is the first. As initially observed in zinc oxide system and suggested by Futsuhara et al., change in ionicity due to the incorporation of **nitrogen atoms is the main reason** for the decreasing band gap values in zinc oxynitrides [46]. Since metal-oxygen (M-O) bonds have a higher ionicity than that of metal-nitrogen (M-N), because the electronegativity of oxygen is higher than that of nitrogen, a decrease in ionicity can be expected in samples with increasing nitrogen incorporation [46].

Thus, the progressing increase in W-N bonds in the mixture of W-O and W-N bonds in W-O-N films with increasing nitrogen content is responsible for the observed E_g decrease. The later explanation, which is a direct consequence of electronic states mixing, is based on the fact that decreasing E_g with nitrogen is due the narrowing of the band gap due to the existence of both the N 2p states with O 2p states simultaneously [43-46]. E_g corresponds to electronic transitions from the top of valence band to the conduction band [2-10]. In WO_3 , the valence band is formed by the filled O 2p states and the conduction band is formed by the empty W 5d states. **The N 2p states are energetically favorable and close to of the O 2p states.** Therefore, with effective nitrogen incorporation, N 2p states intermix with O 2p states of the valence band [45,46]. The overall effect is, thus, valence band expansion with N 2p states occupied above the O 2p states, **resulting in lower E_g values. A proposed electronic structure model, to account for the observed changes in the band gap of W-O-N films, is schematically presented in Figure 8.** The constant values of E_g correspond to a composition that is predominantly WO_3 , where **the electronic transitions correspond to energy gap between valence and conduction bands formed by O 2p and W 5d states, respectively.** The variable, lower band gap in W-O-N corresponds to the electronic transitions from the new valence band, which is formed by a mixture of O 2p and N 2p states. Increases in thenitrogen content, associated with nitrogen flow rates above 9 sccm, as noted in this work, significantly decreases E_g due to valence band expansion and band gap narrowing. **Such phenomena were also reported in other metal oxides with similar band values, for instance in Ti-O-N and Zn-O-N films [43-46].**

5. Conclusions

Amorphous tungsten oxynitride thin films were sputter-deposited by varying nitrogen gas flow rate from 0 to 20 sccm while keeping the total gas flow constant at 40 sccm. XPS and RBS analyses indicate that the nitrogen incorporation is not effective until a nitrogen flow rate of 9 sccm, at which point N 1s peak area increases significantly. Formation of W-O-N films with W-N bonds in addition to W-O bonds significantly influences the optical properties as indicated by spectrophotometry measurements. Optical absorption curves clearly indicate a composite-like phase of W-O-N films. The band gap (E_g) values are highly dependent on the nitrogen content in the reactive gas mixture. Films grown without any nitrogen exhibit $E_g \sim 3.0$ eV, which corresponds to intrinsic WO_3 . E_g decreases continuously to ~ 1.9 eV with increasing nitrogen content in the reactive gas mixture. Electronic structure changes were accounted based on the ionicity of W-O and W-N bonds along with intermixing of N 2p states with O 2p states in the valence band.

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Figure Captions

- Figure 1. GIXRD patterns of W-O-N films deposited at various nitrogen gas flow rates. The amorphous nature of the W-O-N films is evident from the patterns.
- Figure 2. Spectral transmittance curves of W-O-N films deposited at various nitrogen flow rates. Absorption shift with increasing nitrogen flow rate is clearly visible as indicated by the arrow.
- Figure 3. E_g variation of W-O-N films with nitrogen gas flow rate. E_g variation with increasing nitrogen flow rate is a direct indication of changes in the electronic structure of the material with formation of W-O-N films.**
- Figure 4. Extinction coefficient and refractive index plots of W-O-N films for variable nitrogen flow rates. Note the systematic increase in index with respect to increasing nitrogen flow rate.**
- Figure 5. The XPS survey spectrum of W-O-N films deposited at a nitrogen flow rate of 9 sccm. The peaks identified are due to the elements as indicated at their respective BE positions.
- Figure 6. (a) The N 1s peak evolution as a function of nitrogen flow rate. (b) The peak **area** of N 1s peak obtained from high resolution XPS spectra. The data indicates that the nitrogen incorporation and W-O-N film formation is effective from 9 sccm of nitrogen flow rate, which is critical to change band gap as seen from Figure 3.
- Figure 7. RBS spectra of W-O-N films. The data shown are for: (a) pure WO_3 films (i.e., without nitrogen) and (b) W-O-N films deposited at a nitrogen flow rate of 9 sccm. The experimental and simulated (SIMNRA) data are shown for the

samples. The back scattered ions due to various elements present in the samples are as indicated.

Figure 8. Proposed electronic structure model to account for the observed changes in the band gap of W-O-N films. The constant values of E_g corresponds to predominantly WO_3 , where the band gap corresponds to energy gap between valence and conduction bands formed by O 2p and W 5d states, respectively. The variable, lower band gap in W-O-N corresponds to the electronic transitions from the new valence band, which is formed by a mixture of O 2p and N 2p states.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Table 1. Sputtering conditions employed for the deposition of W-O-N thin films.

Physical Parameter	Set Value
Base pressure	3×10^{-7} Torr
Sputtering power	100 W
Processing gases	Ar, N ₂ , O ₂
Substrates	Silicon and quartz
Deposition temperature	Room temperature (25 °C)
Target-to-substrate distance	8 cm
Total gas flow	40 sccm (constant)
Ar gas flow	20 sccm (constant)
N ₂ gas flow	0-20 sccm (variable)
O ₂ gas flow	0-20 sccm (balanced)
Working pressure	10 mTorr
Pumping speed	50 L/s
Deposition rate	20 nm/min
Film thickness	100 nm

Table 2. Tauc-Lorentz oscillator parameters for the fitting of optical constants for W-O-N thin films as a function of nitrogen flow rate.

N₂ flow rate (sccm)	MSE	Thickness (nm)	A	B	E_o (eV)	E_g (eV)
0	6.83	1040.65	54.25	0.04	4.09	2.99
3	5.88	1050.54	45.50	0.30	4.13	2.87
5	4.74	1029.61	32.86	0.45	4.33	2.57
7	2.06	1030.52	18.18	0.45	4.10	2.30
9	1.49	1032.61	15.22	0.66	4.15	2.10
11	1.53	987.31	17.03	1.15	4.25	2.05
13	1.80	1019.65	14.95	1.40	4.15	1.92
15	2.32	1024.23	23.23	2.09	4.13	1.94
17	5.39	978.97	40.51	2.86	3.97	1.89