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Nitrogen incorporation and composition facilitated tailoring of the optical constants and dispersion energy parameters of tungsten oxynitride films

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Optical properties, including the index of refraction, extinction coefficient and band gap of 100 nm thick tungsten oxynitride (W-O-N) films are reported. In addition, the Wemple and DiDomenico (WDD) model was used to calculate the dispersion energies and oscillator energies of the films, establishing a correlation among the films' optical, chemical, and physical properties, as a function of nitrogen content. Nitrogen concentration in the W-O-N films was varied by adjusting the nitrogen gas flow rate from 0 to 20 sccm while keeping total gas flow (nitrogen + oxygen + argon) constant at 40 sccm. Both the index of refraction (n) and extinction coefficient (k) of W-O-N films demonstrated a high degree of sensitivity to the nitrogen content during deposition. The optical constants of films fabricated without any nitrogen correspond to transparent W-oxide (WO_3) where $n_{550} = 2.1$ and $k_{550} = 0.0$. The magnitude of the spectral response for both n and k tends to increase with increasing nitrogen content. Systematic increases of the films' nitrogen content lead to the formation of W-oxide ($E_g \approx 3$ eV) → W-O-N oxynitride semiconductor ($E_g \approx 2$ eV) → N-rich W-O-N semi-metal ($E_g < 2$ eV) → WN_2 type metallic transition was evident in dispersion profiles of n and k for W-O-N films with increasing nitrogen content. The corresponding mechanical characteristics, namely hardness (H) and Young's modulus (E), attain a maximum of 4.46 GPa and 98.5 GPa, respectively, at a nitrogen flow rate of 5 sccm, at which point H and E values decrease to attain 3.57 GPa and 72.91 GPa, respectively. The trend observed in H and E values correlate with the W-O and W-N bonds formation in W-O-N along with the interruption of local epitaxy attributed to increasing nitrogen content within the growth chamber. A correlation among the nitrogen content, optical constants and physical properties, along with the associated dispersion model, is presented to account for the optical properties of sputter-deposited W-O-N films. The results demonstrate that tailoring the properties of W-O-N films for desired applications can be achieved by tuning the nitrogen content and chemical composition.

1. Introduction

Optical and electro-optic (EO) thin films and devices based on transition metal oxynitrides, which combine the mechanical properties of transition metal nitrides with the optical and electrical properties of their counterpart metal oxides, are gaining remarkable recent interest. 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, provide ability to tune the desired properties based on the chemical composition. In addition, oxynitrides can combine the traditional advantages of oxides and nitrides, such as high hardness, oxidation resistance and structural stability at elevated temperatures.

Tungsten oxide (WO_3) is an n-type semiconductor, which exhibits attractive physical, chemical and electronic properties for application in numerous scientific and technological applications in the fields of optics, photovoltaics and optoelectronics [1–10]. WO_3 is commonly referred to as a "chromogenic material" in view of its coloration properties under variable physical and chemical conditions [1–4]. The favorable optical properties described make WO_3 an interesting material, specifically for optics, photovoltaics and

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optoelectronics [1–10]. For instance, WO_3 thin films are often applied in display devices due to their ability to perform oxidation state alterations by field-aided ion intercalation [1–4]. Furthermore, the electronic structure of WO_3 films and nanostructures allow the 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]. When these properties are combined with good charge-transport characteristics, 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 [1–11]. However, WO_3 exhibits absorption in the near ultraviolet and blue regions of the solar spectrum [12–14]. Tuning the band gap of WO_3 is, therefore, critical to extend the absorption to the longer wavelengths in order to increase the photo-electrochemical performance for water splitting by reducing charge recombination and enhanced light absorption [9,14]. One method that has shown significant promise for tuning the band gap of various is the incorporation of nitrogen, which has demonstrated significant effects on the electronic structure of constituent materials. For instance, there were numerous efforts on nitrogen (N) doping into TiO_2 and ZnO illustrating the electronic structure changes [15–20]. Furthermore, efforts directed at doping anions into TiO_2, the very first successful photo-anode, to improve the photoresponse, have proven that N-doping is the most promising approach [15–21]. However, experiments exploring the fabrication and characterization of tungsten oxynitrides (W-O-N) are not as common as Ti-O-N or N-doped ZnO [15–21]. Specifically, while there are some overall efforts on the effect of N-doping on the microstructure, studies focused on the comprehensive understanding of the optical parameters and their dependence on the effective nitrogen content, and the associated electronic structure changes, are scarce. On the other hand, such studies proved to be valuable in deriving a comprehensive understanding of the electronic properties and photochemical performance of Ti- and Zn-based materials. The present work was, therefore, performed on reactively sputter-deposited tungsten oxynitride films. Reactive sputtering enables the user to fabricate high quality films with a large degree of control of chemical composition, structure and thickness, depending on the deposition parameters chosen. Reactive sputtering is also known to improve mechanical properties of transition metal nitride thin films by enabling nitrogen to react with metal to form the metal nitride films.

The objective of the present work is to derive a comprehensive understanding of the optical constants and dispersion energy parameters of W-O-N films with varying nitrogen content. Determination of the optical properties, specifically the index of refraction (n), extinction coefficient (k) and band gap, for oxides and oxynitrides is not only important to study their fundamental optical properties but also to tailor their electrical conductivity to best suit the given practical applications. However, for thin films and nanomaterials, the optical constants and their dispersion profiles are highly sensitive to structure and composition. Optical properties are influenced by various factors such as chemical composition, surface and interface morphologies, crystal structure, packing density, lattice parameters, and defect structure. Therefore, understanding the optical properties of W-O-N, as a function of processing conditions, allows the user to tailor the spectral dispersion of both n and k, providing a road-map for engineering modern electronic and optical devices such as organic solar cells, electro-optic sensors, and optical transistors. In order to investigate the relationship between nitrogen content and optical performance in the W-O-N material system, spectroscopic ellipsometry (SE) has been employed to measure the optical properties of sputter-deposited W-O-N films. SE is a non-destructive method and provides a detailed account of the optical properties of thin films and coatings. The mechanical properties of W-O-N films were also investigated in order to evaluate their hardness and Young's modulus as a function of processing parameters. As presented and discussed in this paper, the results demonstrate that the optical and mechanical properties of W-O-N films can be tailored by tuning the processing conditions.

2. Experimental

W-O-N films were deposited onto clean silicon (Si) (100) substrates by direct current (DC) sputtering. Silicon substrates were cleaned by RCA (Radio Corporation of America) cleaning and were dried before introducing into the vacuum chamber, which had been evacuated to a base pressure of ~3×10^{-7} Torr. A Tungsten (W) target (Plasmaterials Inc.) of 50 mm 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 sputter source at a distance of 80 mm from the substrates. Once an adequate base pressure was reached, 20 sccm of argon was introduced into the chamber and the plasma was ignited at a power of 100 W. For reactive deposition, and to fabricate W-O-N films, oxygen (O_2) and nitrogen (N_2) were employed alongside argon (Ar). 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. While Ar flow was maintained constant at 20 sccm, the net O_2 and N_2 gas flow rates were adjusted to a total of 20 sccm. The effect of the ratio of nitrogen to oxygen was varied in order to understand the effect of nitrogen content on the mechanical and optical properties of W-O-N films. Before each deposition, the target was pre-sputtered for 10 min in Ar with the gun shutter closed. The depositions were carried out at room temperature (25 °C) for a time period sufficient to reach a film thickness of ≈100 nm.

Optical properties were evaluated using spectrophotometric and ellipsometry measurements. Spectroscopic ellipsometry (SE) was performed ex-situ on the films grown on silicon wafers using a J. A. Woollam α-SE instrument. Measurements were done in the range of 381–900 nm with a step size of 2 nm and at angles of incidence of 65°, 70°, and 75°, near the Brewster's angle of silicon. The ellipsometry data analysis was performed using commercially available CompleteEase software [22]. Films grown on optical grade quartz were employed for optical property measurements to probe the transparent nature and band gap of the W-O-N films. Spectrophotometry measurements were made using a Cary 5000 UV-VIS-NR double-beam spectrophotometer.

Mechanical properties, hardness and reduced elastic modulus, of W-O-N films deposited on Si (100) substrates were measured using a traditional nano-indentation method. Load control nano-indentation was performed using a Hysitron TI 750 TriboIndenter employing a Berkovich tip with a 396 nm radius of curvature. Loading and unloading curves were produced by using a maximum load value of 100 μN, which allowed a shallow penetration depth of the W-O-N between 10 nm and 20 nm, depending on the hardness of each respective sample. In order to obtain reliable information and best possible values of mechanical characteristics, 12 indentations were performed on each sample and the results were averaged to a single set of data.

3. Results and discussion

The representative XRD patterns obtained for W-O-N films deposited under variable nitrogen gas flow rate are shown in Fig. 1. All the films exhibit diffuse patterns, the characteristic of