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.

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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 (~2.4–3.2 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 which are predominantly temperature dependent following a sequence of low temperature monoclinic structure, ε-WO_3 below 230 K, triclinic, δ-WO_3 from 230 to 300 K, room temperature monoclinic, γ-WO_3 from 300 to 600 K, ortho-rhombic, β-WO_3 from 600 to 1020 K, and a tetragonal structure, α_1-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

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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 resisters, 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 ~3×10^{-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 W 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 min 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

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

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 Kα 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 Kα 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}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 WO_3 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].