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Optical and chemical properties of mixed-valent rhenium oxide films synthesized by reactive DC magnetron sputtering

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ABSTRACT

Mixed-valent rhenium oxide thin films were deposited using reactive magnetron sputtering employing a metallic rhenium target within an oxygen–argon environment. The oxygen and argon flow rates were systematically varied, while the extinction coefficient, k, of the deposited layers was monitored using *in situ* spectroscopic ellipsometry. *In situ* monitoring was used to identify absorption features specific to ReO_3, namely, the minimization of k brought on by the gap between interband absorption features in the UV at 310 nm and the onset of free electron absorption at wavelengths above 540 nm. Based on these results, oxygen flow ratios of 50% and 60% were shown to produce films having optical properties characteristic of ReO_3, and thus, were selected for detailed *ex situ* characterization. Chemical analysis via X-ray photoelectron spectroscopy confirmed that all films consisted largely of ReO_3, but had some contributions from Re_2O_3, ReO_2 and Re_2O_7. Additional monitoring of the chemistry, as a function of environmental exposure time, indicated a correlation between structural instability and the presence of Re_2O_3 and Re_2O_7 in the films.

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1. Introduction

Rhenium, a hexagonal close packed refractory metal, has several oxides with a variety of interesting optical and electronic properties. The commonly occurring oxides of rhenium are ReO_2, ReO_3, and Re_2O_7 [1–7]. The lowest valence oxide, ReO_2, is monoclinic in structure, while ReO_3 consists of a network of ReO_6 octahedra having a cubic, "perovskite-type" structure [4,8]. Finally, Re_2O_7 consists of ReO_6 octahedra and ReO_4 tetrahedra, and has been reported to be highly hydroscopic, decomposing into perrhenic acid ($HReO_4$) upon exposure to moisture [1,3,9,10]. The most widely investigated of these compounds is ReO_3, due to its metallic-like conductivity and its low absorption within the visible spectrum, both of which are similar to silver [4,11–13]. The high conductivity $\sigma_{ReO3} = 10^3–10^4$ $(\Omega\ cm)^{-1}$ [9,12] and minimal optical absorption are a direct consequence of the electronic configuration of ReO_3, which contains a single free electron within the 5d electron shell [4,8,12,14]. As a result of their unique optical and

electronic properties, thin films of ReO_3 have been used for several diverse applications, including catalysis [10,15–18], interfacial layers for high T_c superconductors [9], anode buffer layers for polymer solar cells [7], and electrical contacts for liquid crystal devices [8]. Additionally, ReO_3 has ultraviolet (UV) absorption features centered at 310, 177, 155, 124 nm (4, 7, 8 and 10 eV), as well as the onset of free-electron absorption at 540 nm (2.3 eV) [4,12,13]. Interestingly, there are no dominant absorption features between 310 and 540 nm (2.3–4 eV), giving rise to a small transmission window within the visible region. Therefore, thin films of ReO_3 could also have promise as a transparent-conductive material in applications requiring a narrow transmission band.

Deposition of mixed-valent rhenium oxide thin films has been performed using radio-frequency (RF) magnetron sputtering [9], electrodeposition [5–7,19,20], evaporation from rhenium filaments [1], and reactive direct current magnetron sputtering (DCMS) [4]. At this time, there have been very few studies on the optical and chemical properties of rhenium–oxygen compounds deposited using reactive DCMS [4], which is the subject of this work. Work by Ghanashyam Krishna et al. has described a method of depositing rhenium–oxygen compounds using reactive DCMS, wherein the bias voltage was varied and its effect on the spectral reflectivity was systematically analyzed [4]. Results obtained by Ghanashyam

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Krishna et al. indicate that it is possible to use reactive DCMS to deposit 50–180 nm thin films that demonstrate optical behavior analogous to bulk ReO_3, as reported by Weaver et al. [12] and Feinlieb et al. [12]. However, to our knowledge, there are currently no studies reporting on the relationship between the chemistry and spectral (380–1700 nm) optical properties of mixed-valent rhenium oxide thin films deposited via reactive DCMS.

Within this study we devise a method of maximizing the ReO_3 content within the films using in situ spectroscopic ellipsometry (iSE). In situ monitoring of the optical behavior, throughout film growth, allows for the selection of oxygen (Q_{O2}) and argon (Q_{Ar}) flow rates capable of increasing ReO_3 content within the films. Process optimization was achieved through real-time identification of characteristic absorption features, namely the minimization of the extinction coefficient, k, at wavelengths between 450 and 750 nm (1.65–2.75 eV). After establishing the deposition conditions required for maximizing ReO_3 content in the films, analyses of their chemical compositions and their oxidation states, were performed using X-ray photoelectron spectroscopy (XPS). In addition to XPS, X-ray reflectivity (XRR) was used to measure the film thickness and density. These XPS and XRR measurements, as well as additional SE measurements, were made ex situ after one and thirty days exposure to atmosphere at ambient temperatures of 20–25 °C and relative humidity between 20% and 25%. Based on the aforementioned reports of instability [1,3,9,10], it is important to analyze environmental robustness prior to using ReO_3 thin films for applications requiring consistent optical performance and structural stability.

2. Materials and methods

2.1. Deposition

Rhenium oxide thin films were deposited within a stainless steel high vacuum chamber evacuated to a pressure of 5.3×10^{-5} Pa (4×10^{-7} Torr). A 3 mm thick, 50 mm diameter rhenium sputter target (99.99%, K.J. Lesker), was magnetically attached to a 50 mm magnetron source (MeiVac, MAK) at an angle of 20° with respect to the substrate normal. The distance between the target and the p-type silicon (1 0 0) (University Wafer LLC) substrate was 9 cm. During deposition, research grade O_2 (99.995%) and Ar (99.999%) were introduced via separate mass flow controllers, mixed prior to entering the chamber, and maintained at a total pressure of 1.33 Pa (10 mTorr) at a pumping speed of 25 L/s [21]. Oxygen and argon content were regulated by controlling the flow rates Q_{O2} and Q_{Ar}, while the total flow rate Q_{TOT} was kept constant at 20 sccm. The oxygen fraction f_{O2}, represented by Q_{O2}/Q_{TOT}, was varied from $f_{O2} = 0.0$–0.8 by increments of 0.1, while the optical constants were monitored every ten seconds using in situ spectroscopic ellipsometry. In situ data were gathered during continuous deposition for a period of one minute at each increment of f_{O2}. Values of f_{O2} resulting in film layers with minimal extinction coefficients throughout the visible region ($400 \leqslant \lambda \leqslant 750$ nm) were selected and used in the deposition of multiple films for further ex situ analysis. The films selected for ex situ optical and chemical analysis were deposited for three minutes at a cathode voltage $V_c = 631$ V and current $I_c = 80$ mA, resulting in an applied power of 50 W. Depositions took place upon a substrate platen set to rotate at 12 RPM to mitigate the anisotropy imparted by the sputtering process. Note that no heating, outside of thermal contributions from the plasma, was applied to the substrate.

2.2. Characterization

The optical constants of the rhenium oxide films were measured using a J.A. Woollam M2000VI spectroscopic ellipsometer (SE) at an angle of incidence of 70°, near the Brewster's angle for silicon. The extinction coefficient (k) and the refractive index (n) were obtained upon fitting the raw polarization data to the Kramer's Kronig consistent model described within Section 3.4. Thickness values obtained through spectroscopic ellipsometry were verified using a KLA-Tencor stylus profilometer.

XPS was performed using a Physical Electronics 5700 equipped with an Al Kα X-ray source operating at 1486.6 eV. The energy scale was calibrated using Au and Cu, according to the procedures outlined by the ISO Standard, ISO 15472. Survey scans were acquired at an analyzer pass energy of 187.85 eV (0.80 eV energy step) while high energy resolution scans of the core level Re 4f, Re 4s, C 1s, and O 1s transitions were acquired at a pass energy of 29.35 eV (0.125 eV energy step). High energy resolution spectra were calibrated with respect to the Re $4f_{7/2}$ transition, corresponding to the Re^{6+} valence state, at a binding energy of 44.9 (±0.1) eV, as reported by Tysoe et al. [1]. This reference energy was used for all films in order to allow for any small electrical charging. To mitigate the level of error present in peak fittings, the spacing between the $4f_{5/2}$ and $4f_{7/2}$ components was constrained to reflect spin–orbit splitting of 2.5 eV [22]. Additionally, the components of the 4f doublets were fit using equal full-width half-maximum values, as well as area ratios of 3:4 ($4f_{5/2}:4f_{7/2}$) [19]. Shirley background subtraction and 70% Gaussian 30% Lorentzian line shapes were used to fit all spectra within the CasaXPS 2.3.16 software package [23]. To obtain a metallic reference for use in quantifying binding energy shifts, some samples were sputtered for 5 min using a differentially pumped ion gun at 4 keV with an argon pressure of 10×10^{-3} Pa and an emission current of 25 mA. The binding energy obtained for the metallic Re^0 $4f_{7/2}$ peak was 40.3 eV. Note that no sputtering was utilized prior to analysis of survey and high resolution scans due to the facile reduction of higher order rhenium–oxygen compounds during sputtering [24,25].

Electron micrographs were taken using an FEI Sirion scanning electron microscope (SEM). Measurements of the films' densities were performed via X-ray reflectivity analysis (XRR) using a Rigaku Smartlab X-ray diffractometer, while grazing incidence X-ray diffraction (GIXRD) was also performed, indicating that all films deposited were amorphous. The observation of the films' amorphous character is in line with results obtained by Hahn et al. for cathodically electrodeposited ReO_3 thin films [6]. In the absence of crystalline character related to various rhenium–oxygen coordination compounds, establishment of the presence of individual compounds was performed through careful analysis of relative charge shifts present within high energy resolution XPS spectra. Further corroboration of the presence of specific compounds, namely ReO_3, was performed through comparison of SE data with data presented within the literature.

3. Results and discussion

3.1. In situ monitoring of optical constants

In situ ellipsometry measurement of rhenium oxide as a function of increasing oxygen content was used in order to determine the oxygen fraction required to minimize the k within the visible region ($400 \leqslant \lambda \leqslant 750$ nm). Since oxides of rhenium are not dielectric, like many transition metal oxides, the onset of arcing and process instability as a function of increasing f_{O2} was not an issue. As shown in Fig. 1, values of k at 450, 600 and 750 nm, are consistent with reported values for metallic rhenium at $f_{O2} = 0.0$ [26]. As f_{O2} is increased, k values continue to decrease until reaching $f_{O2} = 0.4$, where a slight increase in k occurs as the potential result of the onset of absorption features related to lower valent rhenium species [20]. As f_{O2} increases, to 0.5 and 0.6, the target surface begins