Critical-point model dielectric function analysis of WO₃ thin films deposited by atomic layer deposition techniques

Ufuk Kılıç, Derek Sekora, Alyssa Mock, Rafał Korlacki, Elena M. Echeverría, Natale Ianno, Eva Schubert, and Mathias Schubert

1) Department of Electrical and Computer Engineering, University of Nebraska - Lincoln, Lincoln, Nebraska, USA
2) Center for Nanohybrid Functional Materials, University of Nebraska - Lincoln, Lincoln, Nebraska, USA
3) Department of Physics and Astronomy, University of Nebraska - Lincoln, Lincoln, Nebraska, USA
4) Department of Physics, Chemistry, and Biology, IFM, Linköping, University, SE-58183 Linköping, Sweden
5) Leibniz Institute for Polymer Research, Dresden, Germany

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WO₃ thin films were grown by atomic layer deposition and spectroscopic ellipsometry data gathered in the photon energy range of 0.72–8.5 eV and from multiple samples was utilized to determine the frequency dependent complex-valued isotropic dielectric function for WO₃. We employ a critical-point model dielectric function analysis and determine a parameterized set of oscillators and compare the observed critical-point contributions with the vertical transition energy distribution found within the band structure of WO₃ calculated by density functional theory. We investigate surface roughness with atomic force microscopy and compare to ellipsometric determined effective roughness layer thickness.

I. INTRODUCTION

Transition-metal oxides such as tungsten tri-oxide (WO₃) continue to receive increasing interest due to their potential for use in photovoltaics chemical gas sensing, electrochromic smart windows and optical switching applications, for example. Physical vapor deposition (PVD) processes such as sputtering and thermal evaporation techniques and chemical vapor deposition (CVD) processes are convenient to fabricate WO₃ thin films. It has been reported that the electrical, optical, and photocatalytic properties of WO₃ thin films depend crucially on the growth conditions. For example, Subrahmanyam et al. examined the effects of the growth conditions during a sputtering process onto the optical and structural properties of WO₃ thin films. Hao et al. employed a spray pyrolysis method in order to fabricate WO₃ thin films, and investigated changes of their transient photoconductivity properties upon thermal annealing. Gullapalli et al. studied sputter-deposited nanocrystalline WO₃ films, and determined their transmittance and reflectance within the range of 1 eV–4.2 eV. Saenger et al. deposited amorphous WO₃ thin films by magnetron sputtering, and studied their polaron and phonon properties upon reversible electrochemical proton intercalation and reported the dielectric function in the spectral range of 0.037–3.34 eV. The dielectric function can provide insight into optical and electrical properties of a material and has been investigated previously for WO₃ using several methods including ellipsometric techniques. For example, K. von Rottlau et al. utilized ellipsometry and spectrophotometry to investigate the optical constants within the range 0.49 eV–4.13 eV of electrochromic tungsten oxide on ITO coated glass by e-beam evaporation. I. Valuyk et al. fabricated tungsten oxide films by reactive DC magnetron sputtering and performed ellipsometric data analysis based transmittance and reflectance measurements from 0.72 eV–4.13 eV. A. Georg et al. studied WOₓ films with varying crystallinity grown by thermal evaporation comparing optical constants within the range from 0.62 eV–3.72 eV. D. H. Mendelsohn et al., reported on the refractive index and extinction coefficient using ellipsometry in the spectral range 0.5 eV–3.5 eV of polycrystalline electrochromic WO₃ films, grown by RF sputtering. However, to the best of our knowledge, a wide spectral range including ultraviolet to vacuum ultraviolet dielectric function were not yet reported for WO₃ thin films using ellipsometry.

Spectroscopic ellipsometry (SE) is a convenient non-destructive, non-contact optical characterization method, which has been widely employed to study thin films. The interaction between an incident polarized light beam and a stack of layered materials of interest with plane parallel interfaces results in change in the polarization of the reflected or transmitted light beam. The complex-valued ratio, ϱ, taken between incident and reflected or transmitted electric field components of a monochromatic electromagnetic plane waves can be accurately measured in terms of the amplitude ratio, Ψ, and the phase difference, Δ. For isotropic materials and for the case of reflection geometry the relation holds

\[ ϱ = \frac{r_p}{r_s} = \tan (Ψ) e^{iΔ} \]  

where \( r_p \) and \( r_s \) are the Fresnel reflection coefficients for parallel and perpendicular polarized light, respectively.

In order to resolve both thickness and the complex-valued frequency dependent dielectric function of a
In this study, we employ SE to characterize the optical properties of multiple samples using different thickness of WO$_3$ films to the envelope of expected the band-to-band transitions calculated using density functional theory.

II. EXPERIMENTAL DETAILS

Thin films of WO$_3$ were deposited on silicon wafers by plasma-enhanced ALD (Fiji F200, Veeco CNT). The (100) oriented wafers with native oxide were cut from low-doped, p-type conductive, single crystalline silicon. After sample insertion into the reactor, and prior to the main deposition processes, a 300 W oxygen plasma was applied for 300 sec in order to remove residual surface contaminants. Subsequently, a stabilization period was implemented to let the sample reach a steady state temperature. ALD techniques using cyclic exposure to (tBuN)$_2$(Me$_2$N)$_2$W, H$_2$O, and oxygen plasma as described in Ref. [17].

In order to determine elemental and compositional information of our fabricated samples, X-ray photoelectron spectroscopy (XPS) is utilized. The resulting XPS survey spectra corresponding to the samples fabricated with 150 ALD cycles is presented in Fig. 1. The insets of Fig 1 show the spectra for O(1s) and W(4f) core levels. We find that only oxygen and tungsten are present in the film, with a chemical composition of 74.1% and 25.9%, respectively. These values are in good agreement with what is expected for WO$_3$ films.

SE measurements were conducted in the spectral range of 0.72–6.2 eV using a dual rotating compensator ellip-
AFM images were collected from all samples using a multi-mode atomic force microscope (Bruker-Nanoscope III). For all measurements, the field size was chosen to be 2×2 µm with a line resolution of 512×512. The AFM scans were performed in tapping mode with a scan velocity of 0.1 lines per second. Image data were analyzed using Nanoscope Visualization and Analysis software. The model surface roughness parameters of the investigated samples were calculated from the image data, and obtained as Rq, the average of height deviation taken from the mean image data plane, and as Ra, the arithmetic average of the absolute values of the surface height deviations measured from the mean geometric (flat) surface plane.

A density functional theory approach was used for bandstructure calculations. The calculations were performed using the plane-wave density functional theory (DFT) code Quantum ESPRESSO.[29] Atomic coordinates and unit cell parameters were taken from Ref.[30] We used the exchange-correlation functional of Perdew and Zunger[31] and the atoms were represented by Optimized Norm-Conserving Vanderbilt (ONCV) scalar-relativistic pseudopotentials[32] which we generated for the PZ functional using the code ONCVPSP[33] with the optimized parameters of the SG15 distribution of pseudopotentials.[34] The simple monoclinic unit cell containing 8 tungsten atoms and 24 oxygen atoms was first relaxed to force levels less than 10⁻⁹ Ry/Bohr. A regular shifted 2×2×2 Monkhorst-Pack grid was used for sampling of the Brillouin Zone.[35] A convergence threshold of 1×10⁻¹¹ was used to reach self consistency with a large electronic wavefunction cut-off of 100 Ry. For the relaxed structure an additional non-scf calculation was performed in tapping mode with a scan velocity of 0.1 lines per second. Image data were analyzed using Nanoscope Visualization and Analysis software. The model surface roughness parameters of the investigated samples were calculated from the image data, and obtained as Rq, the average of height deviation taken from the mean image data plane, and as Ra, the arithmetic average of the absolute values of the surface height deviations measured from the mean geometric (flat) surface plane.[36]

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strate are presented in Fig. 2, along with the corresponding best match model calculations from the multiple sample analysis. Similar data was obtained for each of the fabricated samples allowing for the extraction of the dielectric function.

The WO₃ layer thicknesses of the investigated samples determined by this MSA approach are presented in Table I. The real and imaginary parts of the spectrally dependent dielectric function, ε₁ and ε₂, determined using a wavelength-by-wavelength regression analysis and are shown as green squares in Fig. 3, together with dielectric function data from selected literature are reproduced into account. Many of the previous studies onto the dielectric function, ε, dependent dielectric function, ε₂, with 75 and 150 ALD cycles showing excellent agreement using extended spectral range unraveled four higher energy CPs in the dielectric function of our ALD fabricated WO₃ ultra thin films.

TABLE I. Thickness parameter results from ellipsometric MSA approach. Parenthesis correspond to the 90% confidence interval obtained from the numerical best-match data analysis.

| Thickness (nm) | Sample I (75 cycles) | Sample II (110 cycles) | Sample III (150 cycles) |
|---------------|----------------------|------------------------|-------------------------|
| d_WO₃         | 6.57(1)              | 10.52(2)               | 14.51(1)                |
| d_R           | 1.48(1)              | 2.09(1)                | 2.38(1)                 |

The resulting dielectric function lineshapes from the critical point analysis are shown in Fig. 3, as red solid lines. Individual contributions to the dielectric function are shown in ε₂. Vertical lines at the determined center energies in both Figs. 2 and 3. Best match model parameters for CP analysis lineshape functions are presented in Table III.

The wide variation in reported band gap energy can also be attributed to variation in deposition methods and conditions with vacuum evaporation seeming to yield the widest band gap. The energy band gap values of selected tungsten oxide thin films which are deposited and optically characterized by different methods are listed in Table II. Unlike the other studies, Ref. 26, in this report, having extended spectral range unraveled four higher energy CPs in the dielectric function of our ALD fabricated WO₃ ultra thin films.

TABLE II. The list of tungsten oxide band gap energy values which is obtained by using different methods.

| Fabrication Method | E_{gap} (eV) |
|--------------------|--------------|
| Ref. 26 reactive DC magnetron sputtering | 3.15 |
| Ref. 48 CVD | 3.25-3.4 |
| Ref. 49 Thermal evaporation | 3.28 |
| Ref. 50 Reactive RF magnetron sputtering | 3.1(1) |
| Ref. 62 Reactive RF magnetron sputtering | 3.08-3.48 |
| Ref. 60 Vacuum evaporation | 3.9 |
| Ref. 61 DFT Calculations | 3.26 |
| Ref. 60 DFT Calculations | 3.46 |

a) G₀W₀ band gap calculations of γ-WO₃ are performed by considering the experimental geometry.

b) This is the energy gap of (WO₃)ₙ where n = 4 cluster.

c) Transition outside investigated region determined with limited sensitivity.

FIG. 4. AFM images of fabricated samples using (a) 75 ALD cycles, (b) 110 ALD cycles and (c) 150 ALD cycles.

Increased thickness of the optical effective roughness layer is observed with increased WO₃ thin film thickness with determined values given in Table II. An increase of approximately 160% is observed between the samples with 75 and 150 ALD cycles. A similar trend is observed in measured surface roughness obtained from AFM image analysis shown in Fig. 4. The values for R_q and R_p are inlaid for each corresponding sample. An increase of approximately 140% is seen in the R_q average and approximately 150% in the R_p average between the samples with 75 and 150 ALD cycles showing excellent agreement with ellipsometric results.

A snapshot of allowed optical transitions in WO₃ was calculated for the most common, monoclinic form of WO₃ and is shown in Fig. 5. All significant allowed transitions regardless of symmetry are plotted. Transitions are observed to fall into several clusters which are spaced in a
similar way to the identified broad CP transitions from the ellipsometric analysis.

IV. CONCLUSIONS

Deposition of WO$_3$ by ALD was performed and spectroscopic ellipsometry was utilized to determine optical properties of the thin films. WO$_3$ thin films with various thicknesses (6.57 nm, 10.52 nm, and 14.51 nm for 75, 110, and 150 cycles, respectively) were investigated using a multiple sample analysis which allowed the thicknesses and optical properties to be decoupled. A comprehensive optical characterization using a critical point analysis was conducted in the wide spectral range of 0.72-8.5 eV and compared with density functional theory calculations. Energetic locations for clusters of DFT calculated allowed transitions agree well with ellipsometric determined energy parameters of critical point features in the dielectric function.

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