Creation and Ordering of Oxygen Vacancies at WO$_{3-\delta}$ and Perovskite Interfaces

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ABSTRACT: Changes in the structure and composition resulting from oxygen deficiency can strongly impact the physical and chemical properties of transition-metal oxides, which may lead to new functionalities for novel electronic devices. Oxygen vacancies (V$_O$) can be readily formed to accommodate the lattice mismatch during epitaxial thin film growth. In this paper, the effects of substrate strain and oxidizing power on the creation and distribution of V$_O$ in WO$_{3-\delta}$ thin films are investigated in detail. An $^{18}$O$_2$ isotope-labeled time-of-flight secondary-ion mass spectrometry study reveals that WO$_{3-\delta}$ films grown on SrTiO$_3$ substrates display a significantly larger oxygen vacancy gradient along the growth direction compared to those grown on LaAlO$_3$ substrates. This result is corroborated by scanning transmission electron microscopy imaging, which reveals a large number of defects close to the interface to accommodate interfacial tensile strain, leading to the ordering of VO and the formation of semi-aligned Magnéli phases. The strain is gradually released and a tetragonal phase with much better crystallinity is observed at the film/vacuum interface. The changes in the structure resulting from oxygen defect creation are shown to have a direct impact on the electronic and optical properties of the films.

KEYWORDS: WO$_p$, epitaxy, oxygen vacancy, defect ordering

INTRODUCTION

Transition-metal oxides (TMOs) form a series of compounds with a wide range of physical and chemical properties and are highly useful in technologies associated with heterogeneous catalysis, electronics, spintronics, and high-temperature superconductivity.1,2 The fabrication of high-quality heterointerfaces with precise control over crystal structure and oxygen stoichiometry is a key challenge hindering our current understanding of the intrinsic properties of TMOs, as well as their broader utilization in next-generation devices. For example, the existence of oxygen vacancies in as-grown SrCrO$_{3-\delta}$ and SrCoO$_{3-\delta}$ films is found to significantly change the structure and physical properties from those of their stoichiometric counterparts.3,4 On the other hand, in many cases, the catalytic properties of TMOs depend on the presence of defects such as oxygen vacancies, dislocations, and grain boundaries, which locally perturb metal–oxygen bonds.5 Thus, the thin film growth community has shown significant interest in tuning the oxygen stoichiometry and defect concentrations by adjusting controllable variables such as growth temperature, oxygen partial pressure, and substrate-induced strain.1,5–8

Stoichiometric tungsten trioxide (WO$_3$) is a semiconductor (~2.8–3.0 eV band gap) that can be easily reduced under electron beam, UV light, or heat treatment.9–11 To better
understand and control the oxygen vacancy concentration, WO₃, is of interest not only for fundamental studies but can also have a direct impact on several important technologies, including electrochromic devices, smart windows, photo-catalysis, and Li-ion batteries. WO₃ crystals generally consist of corner-sharing WO₆ octahedra. The tilting and distortion of WO₆ octahedra lead to several structures, including monoclinic I (γ-WO₃), monoclinic II (ε-WO₃), triclinic (δ-WO₃), orthorhombic (β-WO₃), tetragonal (α-WO₃), and cubic WO₃. Epitaxial WO₃ has been deposited on various lattice-mismatched substrates but the effect of interfacial strain on film structure and properties has not been systematically studied. In contrast to the mechanism of strain relaxation in traditional semiconductors, it has been shown that other relaxation mechanisms, such as rotation/tilt of oxygen octahedra, creation of planar defects, and structural transition, may also play a role in WO₃ epitaxy. Specifically, substoichiometric WO₃ (WO₃−δ) can crystallize in many different forms known as Magnéli phases depending on the extent of oxygen deficiency. These include W₁₂O₃₅ (WO₃δ), W₁₅O₄₇ (WO₃γ), W₁₇O₅₇ (WO₃ε), and W₁₈O₅₈ (WO₃δ). and are characterized by the presence of crystallographic shear planes to accommodate ordered oxygen vacancies through edge sharing among WO₆ octahedra. The relatively simple crystal structure of WO₃ with its small lattice mismatch to commercially available perovskite substrates, and the existing knowledge base for the Magnéli phases make tungsten oxide an ideal model system for studying oxygen vacancy defects.

Our study entails varying the substrate and molecular beam epitaxy (MBE) deposition conditions for epitaxial WO₃−δ films and following the effect(s) that these process variables have on the extent of reduction. Fully stoichiometric WO₃ films are readily deposited on both LaAlO₃ (001) (LAO) and SrTiO₃ (001) (STO) substrates in an ambient of activated oxygen. In contrast, when deposited in an ambient of O₂ at a comparable oxygen partial pressure, the films grown on STO are more oxygen-deficient than those deposited on LAO. The time-of-flight secondary-ion mass spectrometry (ToF-SIMS) studies show no measurable increase in 18O concentration in the film, indicating no further oxidation or oxygen exchange during the deposition of WO₃−δ by congruent evaporation of WO₃ powder in 18O₂. ToF-SIMS also reveals a measurable O concentration gradient within the films, with the film/substrate interface being significant off-stoichiometry (reduced). In combination with high-resolution scanning transmission electron microscopy (STEM), we ascribe this result to the influence of strain. A large number of semi-ordered Magnéli phases are observed near the interface of WO₃−δ and STO. As the strain relaxation occurs at larger thicknesses, the oxygen vacancy concentration drops. The incorporation of oxygen defects is shown to lead to increase in conductivity and coloration of the resultant films. The ability to tune the oxygen vacancy concentration and distribution by interfacial strain and oxidation potential during deposition allows us to better control the electronic and electrochromic properties of WO₃ thin films.

**EXPERIMENTAL SECTION**

The WO₃ thin films were grown in a custom MBE system which has been described elsewhere. High-purity WO₃ powders (Sigma-Aldrich, >99.99%) were evaporated from a high-temperature effusion cell at a film growth rate of ~0.2 Å/s as calibrated by a quartz crystal microbalance. The (001)-oriented LAO and STO (10 × 10 × 0.5 mm, MTI Corporation) substrates were mounted on a 2° sample holder and cleaned at 600 °C for 20 min in an oxygen partial pressure of 6.0 × 10⁻³ Torr prior to film growth. The substrates were heated to 500 °C and were rotated at 1 rpm during the deposition to ensure composition and thickness uniformity. An activated oxygen plasma beam (with O₂ partial pressure in the chamber set at ~3 × 10⁻³ Torr) or an 18O isotope-labeled (Cambridge Isotope Laboratories, Inc., 97%) molecular oxygen (18O₂) beam was incident on the sample during deposition to study the effect of the oxidizing agent on the sample stoichiometry. In situ reflection high-energy electron diffraction (RHEED) was used to monitor the overall morphology and surface structure. After deposition, the substrate temperature was reduced at a rate of 10 °C min⁻¹ under the same oxygen environment. The thicknesses of the films range from 50 to 150 nm.

In situ X-ray photoelectron spectroscopy (XPS) using monochromatic Al Ka X-rays (hv = 1486.6 eV) was carried out at normal emission (electron takeoff angle = 90° relative to the surface plane) with a VG/Scienta SES 3000 electron energy analyzer in an appended chamber. The total energy resolution was 0.5 eV. Spectroscopic ellipsometry measurements have been performed using a commercially available rotating analyzer instrument with a compensator (V-VAZE; J.A. Woollam Co., Inc.) within the spectral range from 0.4 to 4.6 eV. Data have been collected at three incidence angles (50°, 60°, and 70°). The optical band gap E_g can be determined from the absorption coefficient α, calculated using Tauc plot following the equation $E_g = \alpha E_g ^{1/2}$, where α is the absorption coefficient, E is the photon energy, $E_g$ is a constant, and n is equal to 2 for our indirect-gap WO₃ films. The electrical resistivity measurements were performed by the Van der Pauw method using Ag contacts in the temperature range of 150–330 K.

The high-resolution X-ray diffraction (XRD) patterns were recorded using a Philips X'Pert materials research diffractometer equipped with a Cu anode operating at 45 kV and 40 mA, a hybrid monochromator consisting of four-bounce double crystal Ge(220), and a Cu X-ray mirror. ToF-SIMS measurements were performed using a TOF.SIMS5 spectrometer (IONTOF GmbH, Germany). The experimental details are described in a previous paper. In brief, a 2.0 keV Cs⁺ beam was used for sputtering with a sputter area of 300 × 300 μm², whereas a 25 keV Bi⁺ beam was used for data collection, which was scanned on a 100 × 100 μm² area at the center of the Cs⁺ sputter crater. TEM studies were carried out on an FEI Titan 80–300 transmission electron microscope under the scanning mode at 300 kV. The TEM is equipped with a probe corrector and a high-angle annular dark-field (HAADF) detector which enables sub-Angstrom resolution under STEM-HAADF imaging. STEM-HAADF images were collected along the [010] axis by the annular detector in the range of 55–220 mrad with the electron beam convergence angle as 17.8 mrad. Geometric phase analysis (GPA) was conducted using the FRWRTools plugin for Digital Micrograph. An adaptive Wiener filter was applied to the measured STEM-HAADF images and the (001)-type reflections were selected using a mask size of 2.5 nm with a 0.5 smoothing. All strains were calculated relative to the reference region in the substrate; some fluctuation in the strain profile is present at the substrate/film interface because of the abrupt change in contrast.

**RESULTS AND DISCUSSION**

In our earlier work, we demonstrated that WO₃ films deposited in activated oxygen (O plasma) on both STO(001) and LAO(001) are epitaxial and fully stoichiometric, as revealed by in situ RHEED and XPS. The lattice mismatches for cubic WO₃ (α-WO₃ = 3.73 Å) are 1.7% for LAO (α LAO = 3.796 Å) and 4.5% for STO (α STO = 3.905 Å). As a result, a difference in the surface morphology is observed at the initial nucleation stage for films grown on the two substrates, regardless of whether activated molecular oxygen is used. Figure 1a–f displays RHEED patterns for two WO₃ film thicknesses grown on LAO and STO in O₂. The RHEED beam was blanked during the
The faint diffusing spots in WO 3 films have also been observed by several other groups during MBE. They are most likely due to surface reconstruction at low oxygen partial pressure during growth, which has been shown by ex situ x-ray diffraction studies.24–27 XPS was performed on all samples to examine the oxidation states of W. The W 4f core-level photoelectron spectra for the films grown in O 2 on LAO and STO are shown in Figure 1g,h. The spectrum for the film on LAO is elongated, and the RHEED pattern is between spotty and streaky, indicating a smoother surface in comparison to that grown on STO. This difference is most likely because of the smaller lattice mismatch between WO3 and LAO. The islands coalesce to form larger crystals as the thickness of the film increases, which is consistent with the experimental results in MBE. The RHEED patterns for both 50 nm films become spotty and streaky because of less beam transmission and more reflected electrons in the crystal surfaces, as shown in Figure 1c,f. The faint half-order diffraction spots in WO 3 films have also been observed by several other groups during MBE. They are most likely due to surface reconstruction at low oxygen partial pressure during growth, which has been shown by ex situ scanning tunneling microscopy and low-energy electron diffraction studies.24–27

The creation of oxygen defects also affects the crystallographic properties of the films. Figure 2a shows XRD out-of-plane θ=2θ scans around the (200) substrate and film reflections for four films: WO3 on STO and LAO with and without the use of activated oxygen. The four samples are denoted as O_STO, O_LAO, O2_STO, and O2_LAO in the following discussion. All samples exhibit a single Bragg peak near the substrate (002) reflection, confirming epitaxy. The O plasma-treated WO3 films (O_STO and O_LAO) both show an asymmetric, broad peak because of the competition among the three different lattice parameters of the developing monoclinic WO3 phase. As we reported earlier, WO3 films grown under O plasma exhibit a thickness-dependent structural transition from a strained tetragonal phase to its relaxed, bulk monoclinic phase.16 For the films grown in O2 (O2_STO and O2_LAO), the increase in out-of-plane lattice parameter predominantly results from the “chemical expansivity” effect due to the introduction of oxygen vacancies.31–33 The O2_LAO and O2_STO films also show very similar in-plane lattice parameters (3.87 Å), but their (113) in-plane peaks present a doublet at 1.2 eV lower binding energies, revealing the presence of W5+ as a result of oxygen vacancies.11,28,29 From the fitting, the W5+ peak area is ~2% of the total. As each oxygen vacancy donates two electrons, a formula of WO2.99 is extracted from these data. Moreover, the slight reduction also has an impact on the electronic and optical properties of the films. As seen from the XPS valence band (VB) spectrum for the film grown on STO (inset to Figure 1h), a pronounced feature is observed close to the Fermi level. This feature is attributed to the presence of W5+ with a 5d1 configuration resulting from electron donation from oxygen vacancies.11,28–31

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Figure 1. RHEED patterns for LaAlO3(001) and SrTiO3(001) before (a,d) and after 6 nm WO3(001) (b,e) and 50 nm (c,f) WO3(001) film growth. The incident beam was oriented along the [100] direction. Core-level W 4f XPS spectra for two WO3 films grown in O2 on LaAlO3(001) (g) and SrTiO3(001) (h). For the film grown on SrTiO3, a detectable density of states is observed near the Fermi level in the VB spectrum, as seen in the inset of (h).

Figure 2. (a) XRD θ=2θ scans for WO3 films grown on STO in O plasma, STO in O2, LAO in O plasma, and LAO in O2. (b) (113) In-plane scans for two WO3 films of the same thickness grown on O2_LAO and O2_STO. (c) Temperature-dependent resistivity curves for different WO3 films grown in O2. AA denotes the air-annealing. (d) Tauc plot results for WO3 films grown on STO substrates measured before and after air-annealing.
(shown in Figure 2b) reveal the differences in crystallinity. For the same film thickness, the Bragg peak shape for O2-LAO is much more defined and the full width at half-maximum values, 1.3° for O2-LAO and 2.4° for O2-STO, suggests that the crystallite size is roughly twice as large as in the film on LAO. This difference clearly reveals that the O2-LAO film is of higher quality, which agrees with the RHEED observations. The slight reduction of W from 6+ to 5+ revealed in O2-STO with the in-gap state observed at the bottom of the conduction minimum at low defect concentrations. This is also consistent with the in-gap state observed at the bottom of the conduction band by our VB measurement shown in Figure 1b inset. Also in the Tauc plot results (Figure 2d), no obvious change in the band gap (∼2.9 eV) is detected for before and after air-annealing. According to a recent hybrid DFT calculation by Wang et al., this absorption peak can be ascribed to the photoexcited interband transition with an absorption edge at ∼420 nm. To further study the optical properties, we performed ellipsometry measurements on the film grown on STO, as shown in Figure 2d. One extra absorption peak at 0.5–1.2 eV (marked by one blue arrow) is clearly identified in the bluish O2-STO film because of sample reduction, which can be annihilated by air annealing. According to a recent hybrid DFT calculation by Wang et al., this absorption peak can be ascribed to the oxygen vacancy-induced states, which has been shown to reside in the band gap about 0.5–1.0 eV below the conduction band minimum at low defect concentrations. This is also consistent with the in-gap state observed at the bottom of the conduction band by our VB measurement shown in Figure 1b inset. Also in the Tauc plot results (Figure 2d), no obvious change in the band gap (∼2.9 eV) is detected for before and after air-annealing films.

We note that although the XPS results point to complete oxidation for the O2-LAO film, XRD data indicate that it is oxygen-deficient compared to the O2-LAO film, based on the lattice expansion in the c direction. This discrepancy suggests that either the oxygen deficiency level is below the XPS detection limit or the subsurface layers are more reduced than the near-surface region (2–4 nm) probed by XPS. ToF-SIMS and STEM studies reveal that the latter is the correct explanation. Because the O2-STO and O2-LAO samples were grown in O2, ToF-SIMS was employed to investigate the 18O/16O exchange process and the overall oxygen stoichiometry. Figure 3a shows the SIMS depth profile for 18O/O, TiO2, and WO3−δ for a 150 nm thick O2-STO sample. The crossover for the TiO2 and WO3−δ signals determine the position of the interface. The sharpness of the interface was determined by the drop in the WO3−δ signal from 90 to 10% of that measured in the center of the film, which leads to ∼4 nm, a relatively low value for oxide interfaces by SIMS depth profiling. A significant rise in 18O concentration is observed as the TiO2 (WO3−δ) signal starts to increase (drop), revealing that the STO substrate surface is 18O-rich compared to the natural background level (0.205%). This sharp increase is due to the 18O/16O exchange at the STO surface, resulting from the healing of the oxygen vacancies created during high-temperature annealing just before deposition. The 18O concentration is very close to the natural background level in the WO3−δ film, as it is within the STO substrate, indicating that there is neither oxidation of the evolving WO3 film from the ambient gas nor 18O/16O exchange.

Figure 3b plots the normalized O to W ratio (18O/WO3−δ) from ToF-SIMS data for films on both substrates. The normalization was performed by setting the top surface to 3 (2.99) for O2-LAO (O2-STO) according to XPS results. Values lower than 3 indicate oxygen deficiency. While both films show oxygen deficiency toward the film/substrate interface as indicated by the red dotted lines, it is clear that the O2-STO film displays a smaller O/W ratio, indicating that it is more reduced. At the buried interface, the normalized stoichiometry is close to WO3.9 (WO2.8) for O2-LAO (O2-STO). Both substrates thus induce oxygen deficiency close to the interface but not at the surface, which is consistent with O vacancy creation being driven by tensile strain. On the basis of the larger lattice mismatch with STO, it is expected that the WO3/STO interface would be more oxygen-deficient than the WO3/LAO interface, as observed.

To better understand the impact of oxygen stoichiometry on the film structure, the 150 nm O2-STO sample was examined by STEM. The O2-STO film has a flat surface as shown in Figure 4a. The STEM-HAADF image of the WO3−δ/vacuum interface shown in Figure 4b is very similar to that of stoichiometric WO3, demonstrating the excellent crystallinity of the film. The black amorphous region is a carbon coating applied after film growth to protect the film during STEM sample preparation. Near the film vacuum surface, no defects are observed in the STEM image. However, in the vicinity of the film/substrate interface, many kinds of defects can be clearly seen. A misfit dislocation is present in Figure 4c, ∼8 nm from the interface. In addition, several W atom rows are displaced from their ideal pseudo-cubic positions and the local structures are greatly distorted. Similar defects are more common at the film/substrate interface, as shown in Figure 4d,e and marked by an arrow and a square. In our previous study, interfacial defects were found to be caused by the tilting and deformation of WO6 octahedra for stoichiometric O2-STO. For the O2-STO film, the corner-sharing network of WO6 octahedra is interrupted by extensive O vacancy defects. In Figure 4d, each bright spot represents a column of W atoms aligned along the beam direction [010]. It is clear that many of the W columns are shifted away from their pseudo-cubic positions, indicating the ordering of oxygen defects. Such structures are commonly seen in more reduced Magnéli phases, such as W17O47 (WO2.76) and W18O49 (WO2.72) crystal

Figure 3. (a) SIMS depth profiles for a 150 nm O2-STO film grown in O2 on STO. (b) Normalized O/W ratio for two 150 nm thick O2-LAO and O2-STO films during SIMS depth profiling.

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structure, in which corner- and edge-sharing octahedra coexist. Motifs of W\textsubscript{18}O\textsubscript{49} including W rings with pentagonal and hexagonal shapes viewed along the [010] direction are shown in Figure 4c,d. Because many of the W columns shift from their ideal pseudo-cubic positions, it is expected that the W rows will blur along the [001] direction when imaging along the [100] direction. Indeed, because the cubic STO substrate is fourfold symmetric, we have observed other crystal domains where W columns appear as continuous lines instead of sharp spots, as shown in Figure 4e.

A larger-scale STEM-HAADF image shown in Figure 4f reveals that most of the defects (marked by arrows) are located within \(\sim 15\) nm near the film/substrate interface. It is known that these highly defected structures display distinctly different electronic and chemical properties relative to those for stoichiometric WO\textsubscript{3}. To better understand this phenomenon, we have conducted GPA to visualize local strain from our STEM-HAADF images down to the nanometer scale with approximately 0.1% strain resolution. Using this method, we can visualize the strain fields around the defects in the films and explore the possibility of strain relaxation away from the substrate interface. Figure 5a,d shows the STEM-HAADF micrographs of the films used to calculate the strain maps for the O\textsubscript{2}-STO (top row) and O\textsubscript{2}-STO films. Figure 5b,e shows the in-plane strain component (\(\epsilon_{xx}\)) calculated relative to the substrate region marked by the rectangle. These maps clearly indicate the presence of multiple defects extending from the substrate (indicated by the arrows), which are associated with strain fields that extend several nanometers laterally. Figure 5c,f shows the maps of the out-of-plane strain component (\(\epsilon_{yy}\)), overlaid with the average profile integrated parallel to the interface. The films grown in the two oxidizing conditions exhibit a very different behavior. The O\textsubscript{2}-STO film displays a highly compressively strained interface region of \(\epsilon_{yy} \approx -5.5\)% which gradually relaxes toward a smaller value \(\epsilon_{yy} \approx -3.5\)% \(\sim 40\) nm away from the interface. Accompanying this strain release is the transition from highly defected Magnéli structures at the interface region to the pseudo-cubic WO\textsubscript{3} structure. In contrast, the O\textsubscript{2}-STO film exhibits a nearly uniform strain of \(\epsilon_{yy} \approx -5.2\)% averaged over the measured region, which is a direct result of the planar defects formed from WO\textsubscript{6} octahedral distortion in the stoichiometric WO\textsubscript{3} matrix. These results, in conjunction with our other observations, clearly show that local strain can vary greatly as a result of oxygen deficiency. Although the trend of oxygen deficiency along the c direction in the O\textsubscript{2}-STO sample is clearly identified from SIMS and STEM, we expect a similar strain release mechanism, albeit to a much lesser extent, in the O\textsubscript{2}-LAO sample because of a much smaller in-plane...
lattice mismatch (1.7% vs 4.5%). This result qualitatively agrees with the ToF-SIMS findings and explains why sample reduction is not detectable by XPS, which has a probe depth of ≤5 nm. It should also be noted that the high degree of similarity in the c lattice parameter for O2_LAO and O2_STO means that this quantity is not highly sensitive to the extent of oxygen deficiency. As revealed by the SIMS and STEM studies, the major difference in oxygen deficiency between O2_LAO and O2_STO samples is manifested in the in-plane oxygen defects induced by the interfacial strain.

**CONCLUSION**

Using the insight from several experimental methods, we present a detailed investigation into the effects of substrate strain and oxidizing power on the creation and distribution of oxygen vacancy defects in epitaxial WO3−δ. For WO3 deposited on STO in O2, the surface is slightly oxygen-deficient, but the interface is substantially reduced, resulting in the ordering of oxygen vacancies and the formation of semi-aligned Magnéli phases. It is shown that these highly defective structures exhibit lower resistivity and coloration in the films. Thus, by controlling the growth parameters, it is possible to tune the physical properties of the films. In contrast, WO3 deposited on LAO in O2 is substantially less-reduced. From XRD, films grown on both substrates in O2 exhibit a similar degree of expansion along the c axis, indicating that this is not a highly sensitive indicator of oxygen deficiency. ToF-SIMS and STEM studies, combined with XPS and XRD, yield a more complete description of the origin of oxygen vacancies and their spatial distributions, which is critical to understand and control over the properties of functional oxide materials. Deposition in activated oxygen results in complete oxidation of films grown on both substrates. We note that a comprehensive characterization suite is needed to fully understand the nanoscale structure found in the as-grown films. Furthermore, the significant change in the strain state and nanoscale structure found in the as-grown films may exhibit different performance/responses (i.e., electrochromism, thermochromism, and redox activity) when external stimuli are applied.

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**Notes**

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