Unraveling the Structure and Properties of Layered and Mixed ReO$_3$–WO$_3$ Thin Films Deposited by Reactive DC Magnetron Sputtering

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ABSTRACT: Tungsten trioxide (WO$_3$) is a well-known electrochromic material with a wide band gap, while rhenium trioxide (ReO$_3$) is a "covalent metal" with an electrical conductivity comparable to that of pure metals. Since both WO$_3$ and ReO$_3$ oxides have perovskite-type structures, the formation of their solid solutions (ReO$_3$–WO$_3$ or Re$_x$W$_{1-x}$O$_3$) can be expected, which may be of significant academic and industrial interest. In this study, layered WO$_3$/ReO$_3$, ReO$_3$/WO$_3$, and mixed ReO$_3$–WO$_3$ thin films were produced by reactive DC magnetron sputtering and subsequent annealing in air at 450 °C. The structure and properties of the films were characterized by X-ray diffraction, optical spectroscopy, Hall conductivity measurements, conductive atomic force microscopy, scanning and transmission electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray photoemission spectroscopy. First-principles density functional theory calculations were performed for selected compositions of Re$_x$W$_{1-x}$O$_3$ solid solutions to model their crystallographic structure and electronic properties. The calculations predict metallic conductivity and tetragonal distortion of solid solutions in agreement with the experimental results. In contrast to previously reported methods, our approach allows us to produce the WO$_3$–ReO$_3$ alloy with a high Re content (>50%) at moderate temperatures and without the use of high pressures.

INTRODUCTION

Rhenium trioxide (ReO$_3$) is a solid material with a perovskite-type cubic crystalline structure that is formed by a network of regular ReO$_6$ octahedra sharing common vertices in three dimensions with the Re–O–Re angles of 180°. Bulk ReO$_3$ displays metallic behavior with a specific resistivity in the same range as metallic copper, whereas the resistivity of polycrystalline films ReO$_3$ is higher (ρ = 4.0 × 10$^{-3}$ Ωm). ReO$_3$ can be used as a catalyst in organic synthesis, for example, for amide reduction.

Tungsten trioxide (WO$_3$) has a perovskite-type monoclinic crystal structure that can be described as a slightly distorted cubic ReO$_3$-structure, with the corner-shared and tilted WO$_6$ octahedra. Despite the similarities in the structure, WO$_3$ is an insulator with electrochromic properties that are successfully utilized in the production of smart windows. Applications in gas sensing were also reported.

Considering that both materials have a perovskite-type structure and close values of ionic radii of Re$^{6+}$ and W$^{6+}$ in ReO$_3$ and WO$_3$, it should be possible to form solid solutions of mixed ReO$_3$–WO$_3$ (or Re$_x$W$_{1-x}$O$_3$) phases with electronic properties different from those of pure WO$_3$ and ReO$_3$. Finding a well-controllable method for production of such materials would open the route for tweaking and fine-tuning the characteristics of the ReO$_3$–WO$_3$ composite.

WO$_3$/ReO$_3$ heterostructures and WO$_3$–ReO$_3$ solid solutions were studied theoretically in several works. Ling et al. studied the reactivity of hydrogen and methanol on the (001) surfaces of WO$_3$, ReO$_3$, WO$_3$/ReO$_3$, and ReO$_3$/WO$_3$. Additionally, they studied the hypothetical WReO$_6$ structures and found that (001) layered heterostructures are more stable than the mixed ones. Jiang et al. studied coupling between octahedral rotations and local polar displacements in WO$_3$/ReO$_3$ superlattices. They found that superlattices with sufficiently thick ReO$_3$ layers, the absolute number being three or more layers and the rhenium fraction >50%, tend to be more stable than the separated material phases and also show enhanced octahedral rotations in the WO$_3$ layers.

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ReO$_3$ by the deposition of the amorphous WO$_3$ of Re and the formation of ReO$_3$ electronic properties. Our theoretical predictions qualitatively require high pressures and allows high ReO$_3$ content (more than magnetron sputtering and subsequent high temperatures (800°C to the synthesis of ReO$_3$) paper by Helbig et al. describes a new organometallic approach of oxygen-deﬁciency Re$_{3−x}$O$_3$ phases, having the symmetry reduced from cubic to orthorhombic. The second paper by Helbig et al. describes a new organometallic approach to the synthesis of Re$_{1−x}$O$_3$ phases with up to $x = 0.15$. In this work, we developed a novel method to produce layered ReO$_3$/WO$_3$ and mixed ReO$_3$−WO$_3$ thin ﬁlms by reactive DC magnetron sputtering and subsequent ﬁlm annealing in air. In contrast to previously reported methods, our method does not require high pressures and allows high ReO$_3$ content (more than 50%). The crystalline structure of obtained films and their optical and electrical properties were studied by different methods, and the formation of ReO$_3$−WO$_3$ solid solutions was proposed. Additionally, ﬁrst-principles density functional theory (DFT) calculations were performed for selected compositions of Re$_x$W$_{1−x}$O$_3$ solid solutions to model their structural and electronic properties. Our theoretical predictions qualitatively agree with the experimental results.

### EXPERIMENTAL SECTION

**Sample Preparation.** Rhenium oxide and tungsten oxide thin ﬁlms were prepared by reactive DC magnetron sputtering and annealed in air. The targets were a W metal disc (99.9% purity) and a Re metal disc (99.9% purity), which were 50 mm in diameter and 0.3 mm in thickness (GoodFellow). The substrates were 25 × 25 mm fused quartz glasses (SPI Supplies). Magnetron sputtering was performed in the vacuum system SAF25/50 (Sibast) at 50−150 W DC magnetron power in a mixed atmosphere of sputtering Ar gas (20 sccm) and reactive O$_2$ gas (10 sccm) at a total pressure of 20 mTorr. The substrate was mounted 15 cm above the magnetrons and maintained at room temperature during the deposition process.

Eight samples were prepared in total. Sample #1 was prepared by the deposition of the amorphous WO$_3$ film, followed by annealing for 1 h at 450 °C. Samples #2, #3, #4, and #5 had two layers: samples #2 and #3 have WO$_3$ as the ﬁrst layer, while samples #4 and #5 have ReO$_3$ as the ﬁrst layer. Sample #2 was prepared by the deposition of the amorphous WO$_3$ as the ﬁrst layer and the amorphous ReO$_3$ as the second layer, following by annealing for 30 min at 300 °C. During annealing, all these and subsequent samples were capped by quartz glass to prevent ReO$_3$ sublimation. Sample #3 was prepared by the deposition of the amorphous WO$_3$ as the ﬁrst layer and the amorphous ReO$_3$ as the second layer, followed by annealing for 30 min at 450 °C. Sample #4 was prepared by the deposition of the amorphous WO$_3$ as the ﬁrst layer and the amorphous ReO$_3$ as the second layer, followed by annealing for 30 min at 450 °C. After deposition of the second layer of amorphous WO$_3$ the sample was annealed for 30 min at 450 °C. Sample #5 was prepared by the deposition of the amorphous ReO$_3$ as the ﬁrst layer and amorphous WO$_3$ of the second layer, followed by annealing for 30 min at 450 °C. Samples #6, #7, and #8 were prepared by simultaneous deposition of WO$_3$ and ReO$_3$ with different Re/W ratios. The fabrication of the samples is summarized in Table 1.

**Sample Characterization.** The structure and crystallinity of the ﬁlms were determined by the X-ray diffraction (XRD) technique. The XRD patterns were recorded using a benchtop Rigaku MiniFlex 600 powder diffractometer. Rietveld reﬁnement was performed with BGMN software using the Profex code. The ﬁlm morphology was studied with a scanning electron microscope SEM/FIB Lyra XM (Tescan). The crystalline structure of the ﬁlms was imaged using a transmission electron microscope TEM/FIB Lyra XM (Tescan). The crystalline structure of the ﬁlms was imaged using a scanning transmission electron microscope (STEM) (Tecnai G2F20, FEI) operated at a 200 kV accelerating voltage. The electrical parameters were measured in the van der Pauw conﬁguration using a Hall effect system, HMM5000 (Ecopia). Topography and related electric current maps were obtained in the contact mode by an atomic force microscope (AFM) Park NX10 (Park Systems). Optical reﬂection and transmission spectra were measured using a spectrophotometer Cary 7000 (Agilent). X-ray photoemission spectroscopy (XPS) measurements were performed using an X-ray photoelectron spectrometer ESCALAB Xi (Thermo Fisher), and XPSPEAK41 software was used for peak ﬁtting. Raman scattering spectra were recorded in back-scattering geometry using a TriVista777 confocal micro-Raman system (Princeton).

### Table 1. Description of Sample Preparation Sequence, Film Thickness, Composition, and Macroporous Resistivity

| Sample no. | Description of preparation sequence | Thickness, nm | Resistivity, Ω/sq |
|------------|------------------------------------|--------------|------------------|
| 1          | Single layer: amorphous WO$_3$ thin film; annealing: 1 h at 450 °C | WO$_3$: 120 |               |
| 2          | First layer: amorphous WO$_3$ (100 nm); second layer: amorphous ReO$_3$ (100 nm); annealing: heated for 30 min at 300 °C | WO$_3$: 125 | 1.2 × 10$^3$ |
| 3          | First layer: amorphous WO$_3$ (100 nm); second layer: amorphous ReO$_3$ (100 nm); annealing: heated for 30 min at 450 °C | ReO$_3$: 100 | 1.4 × 10$^4$ |
| 4          | First layer: amorphous ReO$_3$ (100 nm); annealing 1: heated for 30 min at 300 °C | ReO$_3$: 100 | 5.3 × 10$^4$ |
| 5          | Second layer: amorphous WO$_3$ (100 nm); annealing 2: heated for 30 min at 450 °C | WO$_3$: 135 | 2.3 × 10$^4$ |
| 6          | Simultaneous deposition of ReO$_3$ and WO$_3$ (Re/W ratio 1:1); annealing: heated for 30 min at 450 °C | ReO$_3$−WO$_3$: 365 |               |
| 7          | Simultaneous deposition of ReO$_3$ and WO$_3$ (Re/W ratio 1:2); annealing: heated for 30 min at 450 °C | ReO$_3$−WO$_3$: 300 | 1.4 × 10$^6$ |
| 8          | Simultaneous deposition of ReO$_3$ and WO$_3$ (Re/W ratio 3:1); annealing: heated for 30 min at 450 °C | ReO$_3$−WO$_3$: 355 | 2 × 10$^7$ |

*Resistivity is too high to be measured by our system.*
In view of the same spectra in regions 2 and 3, monoclinic (Pm3m) and several known WO3 phases. A good agreement was found with the available experimental data and previous first-principles calculations. The calculations of mixed ReO3–WO3 solid solutions were performed using 2 × 2 × 2 supercells containing eight chemical formulas with removed symmetry and a fully relaxed structure.

## RESULTS AND DISCUSSION

### X-ray Diffraction Analysis

The X-ray diffraction patterns of WO3–ReO3 thin film samples are shown in Figure 1a,b. Their analysis by Rietveld refinement is reported in the Supporting Information, Table S1. The XRD pattern of sample #1 (pure WO3 thin film) corresponds to the monoclinic (P21/n) WO3 phase. Sample #2 has good crystallinity and is composed of a cubic (Pm3m) ReO3 phase. A mixture of cubic ReO3 and monoclinic (P21/n) WO3 phases with a reduced crystallite size was found in samples #3 and #4. Samples #5, #6, #7, and #8 correspond to the WO3–ReO3 solid solutions, and their XRD patterns were refined using the tetragonal (P4/mmm) phase. The reduction of lattice symmetry down to tetragonal is responsible for the appearance of two small peaks at 2θ = 29 and 45°, which are absent in the cubic phase. The smallest crystallite size of about 17–27 nm was found in samples #5, #6, and #7. At the highest rhenium content in sample #8, the crystallite size increases to about 95 nm, and the pattern looks close to that of a cubic (Pm3m) ReO3 phase. However, also, in this case, the tetragonal (P4/mmm) phase gives a slightly better agreement. The lattice constants of the tetragonal solid solutions with different compositions do not deviate too much and are equal to a = 5.274–5.313 Å and c = 3.748–3.753 Å.

It is interesting to note that samples #2 and #3 have an identical composition after film deposition (WO3/ReO3), with the only difference in the annealing temperature (300 °C for sample #2 and 450 °C for sample #3). Only the ReO3 peaks were visible on the XRD spectrum of sample #2 because the annealing temperature was not sufficiently high to crystallize the amorphous WO3 layer (Figure 1a,b). While both ReO3 and WO3 phases are visible on the XRD spectrum of sample #3. Samples #4 and #5 had a very similar composition (ReO3/WO3) but different XRD patterns (Figure 1a,b). In sample #4, the rhenium oxide layer was crystallized and converted into ReO3 before deposition of the upper WO3 layer; while in sample #5, the rhenium oxide layer was amorphous before deposition of the upper WO3 layer. Rietveld analysis of XRD spectra of sample #4 reveals two separate cubic ReO3 and monoclinic WO3 phases, while the spectra of sample #5 show a single tetragonal phase attributed to the Re2W6-xO3 solid solution (Table 2). We explain the different behavior of these samples during the annealing process by higher volatility of amorphous rhenium oxide and the ability to interact with amorphous WO3 in comparison to crystalline ReO3.

### Transmission Electron Microscopy

For investigation of the thin-film morphology in cross sections, transmission electron microscopy (TEM) lamellas were prepared using focused ion beam scanning electron microscopy (SEM-FIB) and are shown in Figure S3 (Supporting Information). TEM was used to determine the thickness of thin film layers (Table 1) and to investigate the degree of crystallinity of obtained samples. At the cross section of samples #2 and #3, one can see the bottom WO3 layer and upper ReO3 layer (Figure S3b,c). For samples #4 and #5, ReO3 is the bottom layer and empty lacunas can be seen on both samples in Figure S3d,e, while the upper WO3 layer remains compact. Lacunas are formed due to sublimation and diffusion of rhenium oxide. For mixed WO3–ReO3 samples #6, #7, and #8, the film material is homogeneous (Figure S3f,g,h). The most important information about mixed samples #6, #7, and #8 is the high degree of crystallinity of these films. The crystallographic phase of these mixed ReO3–WO3 samples was identified as tetragonal P4/mmm and interpreted as Re2W6–xO3 solid solution (Table 2). At high magnification TEM images, one can see crystals and atomic structure of samples #6, #7, and #8 (Figure 2). The biggest crystallite size among mixed ReO3–WO3 samples demonstrate sample #8, which well corresponds with Rietveld analysis (Table 2).

### Optical Properties

Sample #1 (pure WO3 thin film) was highly transparent compared to other works (Figure 3a). All other samples containing rhenium (samples #2–8) were significantly less transparent in comparison to pure WO3. Their transparency is reversely correlated with the Re content, with a maximal transmittance window in the region around 500 nm (Figure 3b). Visually, all samples containing Re were green-blue in transmitted light (Supporting Information, Figure S1). Maximum transparency of Re-containing samples is close to the transparency window of pure ReO3, which is in the spectral range of 475–525 nm (Figure S2 in the Supporting Information). In spite of the same composition, sample #3 is more transparent in comparison to sample #2 due to partial sublimation of rhenium oxide. The spectrum of sample #5 shifted a bit to shorter wavelength in comparison to the spectrum of sample #4. The transmittance window of the spectra of samples #6, #7, and #8 is shifted to shorter...
Table 2. Rietveld Analysis of the XRD Patterns of WO3 and Mixed ReO3–WO3 Thin Films

| sample no. | phase 1                  | phase 2                  |
|-----------|--------------------------|--------------------------|
| 1         | 100% WO3                 | P21/c monoclinic         |
|           | a = 7.322 ± 0.001 Å      | a = 7.444 ± 0.002 Å      |
|           | b = 7.544 ± 0.002 Å      | c = 7.682 ± 0.002 Å      |
|           | d = 66 ± 3 nm            | d = 66 ± 3 nm            |
| 2         | 100% ReO3, Pn3n cubic   | 75% WO3, P21/c monoclinic |
|           | a = 3.7508 ± 0.0001 Å    | a = 7.319 ± 0.001 Å      |
|           | d = 464 ± 30 nm          | b = 7.500 ± 0.002 Å      |
| 3         | 25% ReO3, Pn3m cubic    | 25% WO3, P21/c monoclinic |
|           | a = 3.7506 ± 0.0002 Å    | a = 7.346 ± 0.001 Å      |
|           | d = 129 ± 10 nm          | b = 7.615 ± 0.002 Å      |
| 4         | 43% ReO3, Pn3m cubic    | 43% WO3, P21/c monoclinic |
|           | a = 3.7515 ± 0.0002 Å    | a = 7.346 ± 0.001 Å      |
|           | d = 118 ± 6 nm           | b = 7.615 ± 0.002 Å      |
| 5         | 100% ReW1−xO3, P4/mmm tetragonal |
|           | a = 5.305 ± 0.002 Å      | c = 3.753 ± 0.004 Å      |
|           | d = 20 ± 2 nm            | d = 20 ± 2 nm            |
| 6         | 100% ReW1−xO3, P4/mmm tetragonal |
|           | a = 5.274 ± 0.001 Å      | c = 3.794 ± 0.001 Å      |
|           | d = 27 ± 2 nm            | d = 27 ± 2 nm            |
| 7         | 100% ReW1−xO3, P4/mmm tetragonal |
|           | a = 5.302 ± 0.001 Å      | c = 3.748 ± 0.002 Å      |
|           | d = 17 ± 2 nm            | d = 17 ± 2 nm            |
| 8         | 100% ReW1−xO3, P4/mmm tetragonal |
|           | a = 5.313 ± 0.003 Å      | c = 3.756 ± 0.002 Å      |
|           | d = 95 ± 2 nm            | d = 95 ± 2 nm            |

aSpace group, lattice parameters (a,b,c), and the crystallite size (d) are reported.

wavelength; transmittance is reversely correlated with the Re content (Re/W ratio for sample #6, #7, #8 is 1:7, 1:2, 3:1).

Raman Spectroscopy. Raman scattering spectra of WO3–ReO3 thin film samples are reported in Figure 4. The appearance of the crystalline WO3 phase in the as-prepared films depends on the heat treatment process used during their preparation (Figure 4). The metallic layer of cubic ReO3 located at the top of samples #1 and #2 screens the Raman signal from the bottom WO3 phase, which is crystalline in sample #1 but amorphous in sample #2. The strong Raman signal in sample #3 is due to the crystallized WO3 phase (a set of sharp bands at about 132, 270, 328, 607, 714, and 806 cm−1 are attributed to the triclinic WO3 δ-phase1,32,32), while rhenium oxide was evaporated from the sample surface upon heating at 450 °C. In samples #4 and #5, the top layer of tungsten trioxide protects the rhenium oxide sublayer from evaporation. Their Raman spectra are similar and include three main broad bands at 400–500, 500–850, and 850–1050 cm−1 additionally to a weak band from the WO3 phase at about 800 cm−1. The latter disappears in the mixed samples #6, #7, and #8, while the three broad bands remain clearly visible. Note that the intensity of the three broad bands is reduced in samples #7 and #8.

Since cubic ReO3 shows no or weak Raman activity,33 the observed sharp peaks in all Raman spectra are related to the WO3 phase. However, the three broad bands at 400–500, 500–850, and about 950 cm−1 in samples #4–#8 are attributed to the WO3–ReO3 solid solutions with a tetragonal lattice, which are formed in the films according to our XRD data (Figure 1). Note that the broad band at 950 cm−1 is well observed in all as-prepared samples #4, #5, and #6 but is weaker in samples #7 and #8 with a lower tungsten content. In the literature on different tungsten oxide phases, the origin of this band is usually attributed to the presence of the W=O double bonds. In crystalline tungsten trioxide hydrates, the band at about 950 cm−1 appears as a relatively sharp peak and is ascribed to the stretching mode of the terminal W=O double bond.34 In amorphous tungsten oxide thin films, the band at about 950 cm−1 has been studied in the past by many authors and is also attributed to the W=O stretching mode.35 At the same time, a weak band located at close wavenumbers was found in ground WO3 powders and WO3–ReO3 mixtures,39 where it was attributed to reduced tungsten ions W6−x3+ making tungsten–oxygen bonds at the oxide surface or the interface between WO3 and ReO3 phases.

We do not expect to have a significant amount (if any) of W=O bonds in our samples of WO3–ReO3 solid solutions. Note that the Raman spectrum of sample #6 is similar to that of the tungsten oxide sample studied in ref 40 and attributed to the cubic c-WO3 phase produced by the low-temperature (around 250 °C) decomposition of WO3·2H2O. However, it is possible that the cubic c-WO3 phase in ref 40 is indeed tetragonal and was misinterpreted due to the low quality of its XRD pattern.
Moreover, the XRD patterns of samples produced using the same technology in ref 41 were qualitatively interpreted to be due to cubic or orthorhombic tungsten oxide phases, but again not all peaks in the XRD pattern of the cubic c-WO$_3$ phase were assigned. At the same time, the cubic c-WO$_3$ sample synthesized at high pressure and temperature in ref 42 demonstrates good quality XRD pattern refined in space group Pnma but its Raman spectrum is different from that in ref 40 and our spectra in Figure 3a. Thus, the origin of the band at 950 cm$^{-1}$ in our samples is still obscure.

The correlation between the 950 cm$^{-1}$ band intensity and the amount of tungsten in WO$_3$–ReO$_3$ solid solutions allows us to assume that the band is related to the tungsten sublattice. Note that the W–O phonon modes with large (>900 cm$^{-1}$) wavenumber values exist in all pure WO$_3$ phases but they are not Raman active. Therefore, we propose that an increase of the unit cell and the presence of rhenium ions in the solid solutions may lead to the activation of new Raman modes.

**X-ray Photoelectron Spectroscopy.** An XPS study was performed to qualitatively determine the composition of the surface of the thin film and analyze the oxidation states of the Re and W ions. High-resolution spectra of the Re 4f and W 4f peaks were acquired for each sample (Figure 5). The XPS spectrum of sample #1 shows the presence of the W signal: a doublet of 4f$^7$/2 and 4f$^5$/2 at the binding energies of 35.8 and 37.6 eV due to the spin–orbit splitting indicates the presence of W$^{6+}$ in the film. The spectrum of sample #2 (quartz/WO$_3$/ReO$_3$ annealed at 300 °C) exhibits only the Re signal (Figure 5b), which is present in two oxidation states: Re doublet 4f$^7$/2 and 4f$^5$/2 peak energies at binding energies of 43.5 and 46.0 eV correspond to the 6+ and 7+ oxidation states, respectively, indicating the presence of ReO$_3$ and Re$_2$O$_7$ compounds on the surface of the film. Sample #3 (quartz/WO$_3$/ReO$_3$ annealed at 450 °C) has signals from both Re and W (Figure 5c): the spectrum of rhenium is similar to the previous sample. The spectrum of W indicates the presence of W$^{6+}$ in the film. The spectra of the samples #4 and #5 (quartz/c-ReO$_3$/WO$_3$ and quartz/a-ReO$_3$/WO$_3$ annealed at 450 °C) are almost identical (Figure 5d, e): a strong signal of W 4f doublet peaks characteristic for W$^{6+}$ and a weak signal of Re 4f doublet peaks for Re$^{7+}$ are visible. Sample #6 (mixed WO$_3$–ReO$_3$ annealed at 450 °C, Re/W ratio 1:7) also demonstrates a strong signal of W 4f doublet for W$^{6+}$ and a weak signal of Re 4f doublet for Re$^{7+}$ and Re$^{6+}$ (Figure 5f). The spectra of the samples #7 and #8 (mixed WO$_3$–ReO$_3$ annealed at 450 °C, Re/W ratio 1:2 and 3:1, respectively) also demonstrate strong signals of Re 4f doublets for Re$^{7+}$ and Re$^{6+}$ and W 4f doublet for W$^{6+}$ and W$^{5+}$ (Figure 5g, h). The presence of the Re$^{7+}$ signal on the surface of samples #4 and #5 confirms that Re atoms sublime from the bottom Re layer and diffuse through the W layer to the sample surface.

**Electrical Properties.** Macroscopic electrical resistivity of the WO$_3$–ReO$_3$ films was measured at room temperature in the van der Pauw configuration using a Hall measurement system. Current–voltage characteristics were linear for all samples, indicating good ohmic contacts. The resistivity of samples #1 and #6 was too high to be measured by our Hall measurement system. The obtained data are summarized in Table 1. Note, that samples #2, #3, #4, #5 consist of two layers (ReO$_3$ and WO$_3$), and conductivity is due to mainly the ReO$_3$ layer. The minimal resistivity was demonstrated by sample #2 (WO$_3$/ReO$_3$ sample heated at 300 °C), where ReO$_3$ is the upper layer, and the annealing temperature is optimal for the crystallization of ReO$_3$. However, this temperature is not high enough for the crystallization of WO$_3$ (see XRD spectrum in Figure 1). The resistivity of sample #3 (WO$_3$/ReO$_3$ sample heated at 450 °C) is significantly higher in comparison to sample #2 due to partial sublimation of ReO$_3$. Samples #4 and #5 (ReO$_3$/WO$_3$ heated at 450 °C) have comparable resistivity; however, sample #5 is two times more conductive than #4. Samples #6, #7, and #8 were prepared by simultaneous deposition of rhenium and tungsten oxides and annealed at 450 °C; resistivity of these samples is reversely dependent on rhenium content and is equal to 0.7 Ωm for sample #7 and 7 × 10$^{-2}$ Ωm for sample #8 (resistivity of...
sample #6 was too high to be measured by our system). The only available data on ReO$_3$–WO$_3$ solid solutions resistivity was published by Sleight and Gillson,\textsuperscript{11} who reported the electrical resistivity of ReO$_3$–3WO$_3$ bulk crystals equal to $3.4 \times 10^{-5}$ Ωm, while the electrical resistivity of pure ReO$_3$ bulk crystals $3.6 \times 10^{-7}$ to $8 \times 10^{-8}$ Ωm depending on the synthesis method.\textsuperscript{11} In our previous work,\textsuperscript{3} we found minimal electrical resistivity of pure ReO$_3$ thin films prepared at 250 °C equal to $4.0 \times 10^{-7}$ Ωm with the tendency to increase at a higher annealing temperature to $1.3 \times 10^{-5}$ Ωm at 350 °C. In this work, we use an annealing temperature of 450 °C to achieve ReO$_3$–WO$_3$ film crystallization, which was impossible at 250 and 350 °C.

**Conductive AFM.** All samples were investigated using conductive AFM to study the electrical properties at a microscopic scale. Sample #1 or pure WO$_3$ thin film has a very high electrical resistance of $3.8 \times 10^{11}$ Ω (Figure 6b). Sample #3 having the WO$_3$ bottom layer and the ReO$_3$ upper layer demonstrates a lower resistance of $4 \times 10^8$ Ω (Figure 6d).

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**Figure 5.** XPS spectra for sample #1 (a), sample #2 (b), sample #3 (c), sample #4 (d), sample #5 (e), sample #6 (f), sample #7 (g), and sample #7 (h).
Samples #4 and #5 have the ReO$_3$ bottom layer and the WO$_3$ upper layer and show high resistance values of 1.6 × 10$^9$ Ω and 2.5 × 10$^9$ Ω, respectively (Figure 6f,h). The resistance of samples #4 and #5 is significantly lower (at least 2 orders of magnitude) in comparison to sample #1. We suggest rhenium oxide diffusion from the bottom of the ReO$_3$ layer through the upper WO$_3$ layer. XPS spectroscopy and tomography data confirm this hypothesis.

Mixed ReO$_3$–WO$_3$ samples #6, #7, and #8 show resistance higher than that of sample #3 (having an upper ReO$_3$ layer) and lower in comparison to samples #4 and #5 (having an upper WO$_3$ layer): 1.5 × 10$^8$, 1.1 × 10$^7$, and 1 × 10$^7$ Ω, respectively (Figure 7). In other words, the resistivity of mixed ReO$_3$–WO$_3$ samples is in between WO$_3$ and ReO$_3$ film resistivity. The conductivity map of mixed ReO$_3$–WO$_3$ samples demonstrates good homogeneity with the inclusion of small non-conductive regions (discussed later).

SEM Analysis. The surface morphology was studied using SEM. Randomly oriented closely packed ReO$_3$ crystallites of submicrometer size are visible on the surface of sample #2 (Figure 8a). ReO$_3$ crystallites are not closely packed on the surface of sample #3, probably due to the partial sublimation of the ReO$_3$ material (Figure 8b). The surface of samples #4 and #5 looks very close, showing a nanocrystalline surface with some arbitrarily shaped crystallites of submicrometer size.

SEM images of mixed WO$_3$ and ReO$_3$ thin film samples #6, #7, and #8 are shown in Figure 9. The surface of sample #6 is
smooth and featureless, while samples #7 and #8 demonstrate similar small rectangular-shaped crystals.

There are three types of microcrystals visible on AFM and SEM images. First one is pure ReO$_3$ microcrystals with an arbitrary shape, as shown in Figure 8a,b (can be seen on sample #2 and #3). On the surface of pure ReO$_3$ thin films annealed at 250−300 °C, these microcrystals have a cubic shape, but at a higher annealing temperature, the shape changes due to sublimation. The second type of crystals is nonconductive and can be seen in AFM images: Figures 6c−h and 7a−d. In SEM images, these microcrystals appear as black crystals, Figure 8c,d. We believe that these are HReO$_4$ crystals, which appear at the ReO$_3$ containing surface upon exposure to humid air. In Re$_0.875$W$_0.125$O$_3$, the shape of the supercell is cubic, and both rhenium and tungsten ions are located within the regular octahedra. The W−O bond length is slightly longer (by 0.02 Å) than that of Re−O. However, already in Re$_0.75$W$_0.25$O$_3$, the early evidence of the tetragonal distortion starts to appear as slightly non-equivalent Re−O bond lengths. In Re$_0.5$W$_0.5$O$_3$ solid solution, the difference between $a$, $b$, and $c$ lattice parameters and the axial distortion of the WO$_6$ and ReO$_6$ octahedra is well observed and indicates the tetragonal distortion of the lattice. At lower rhenium concentration (Re$_0.25$W$_0.75$O$_3$), the lattice distortion increases further, promoting the rotation of the metal−oxygen octahedra and off-center displacements of metal ions (Figure 10). The tetragonality of the lattice is well reflected in the lattice parameters with $c$ being larger than $a$ and $b$. Thus, our first-principles DFT calculations suggest that the addition of tungsten to ReO$_3$ induces the tetragonal distortion of the lattice in agreement with the XRD results discussed above.

First-Principles DFT Calculations. The results of the first-principles calculations performed within a $2 \times 2 \times 2$ supercell model with removed symmetry and full relaxation of the lattice constants and atomic fractional coordinates are shown in Figure 10 for selected Re$_{1-x}$W$_x$O$_3$ solid solutions, which cover the full range of compositions studied experimentally. While our model is rather simple, it predicts the behavior of the cubic ReO$_3$ structure upon substitution of rhenium atoms with tungsten ones. For all studied compositions, the Fermi level is located in the conduction band, suggesting their metallic conductivity. The bottom of the conduction band is mainly due to the 5$d(t_{2g})$-states of rhenium and tungsten ions, and the conduction band becomes broadened for the low tungsten content.

In pure WO$_3$, the conduction band is separated from the valence band by a gap, whose size depends on the oxide phase. Our calculations (Figure S6) suggest that the band gap increases from about 2.3 eV in cubic WO$_3$ (Pm3m) to 3.7 eV in orthorhombic (Pbnm) and 4.1 eV in triclinic (P$ar{1}$) WO$_3$ phases. These results are in good qualitative agreement with previous theoretical studies. In solid solutions with a high tungsten content (Re$_{0.125}$W$_{0.875}$O$_3$), the calculations predict a separation (a gap) of about 2.2 eV between the top of the 2$p$(O) states and the bottom of 5$d$(Re/W)-states. Upon increasing the rhenium concentration, this gap decreases down to about 0.6 eV in Re$_{0.875}$W$_{0.125}$O$_3$ and is equal to 0.4 eV for pure cubic ReO$_3$. Thus, the value of the gap between the 2$p$(O) and 5$d$(Re/W)-states in Re$_{1-x}$W$_x$O$_3$ solid solutions is between that for pure WO$_3$ and ReO$_3$ phases. The Mulliken population analysis indicates that the charges on rhenium and tungsten ions decrease slightly from $Z$(Re) = +2.76 and $Z$(W) = +2.81 in Re$_{0.125}$W$_{0.875}$O$_3$ to $Z$(Re) = +2.70 and $Z$(W) = +2.77 in Re$_{0.875}$W$_{0.125}$O$_3$ as a result of electron delocalization.

The most intriguing result of our calculations is the strong evidence of the supercell tetragonal distortion occurring upon an increase of the tungsten content (Table S1), which is also found by the Rietveld refinement of the experimental diffraction patterns (Figure 1 and Table S2). At a large rhenium concentration (Re$_{0.875}$W$_{0.125}$O$_3$), the shape of the supercell is cubic, and both rhenium and tungsten ions are located within the regular octahedra. The W−O bond length is slightly longer (by 0.02 Å) than that of Re−O. However, already in Re$_{0.75}$W$_{0.25}$O$_3$, the early evidence of the tetragonal distortion starts to appear as slightly non-equivalent Re−O bond lengths. In Re$_{0.5}$W$_{0.5}$O$_3$ solid solution, the difference between $a$, $b$, and $c$ lattice parameters and the axial distortion of the WO$_6$ and ReO$_6$ octahedra is well observed and indicates the tetragonal distortion of the lattice. At lower rhenium concentration (Re$_{0.25}$W$_{0.75}$O$_3$), the lattice distortion increases further, promoting the rotation of the metal−oxygen octahedra and off-center displacements of metal ions (Figure 10). The tetragonality of the lattice is well reflected in the lattice parameters with $c$ being larger than $a$ and $b$. Thus, our first-principles DFT calculations suggest that the addition of tungsten to ReO$_3$ induces the tetragonal distortion of the lattice in agreement with the XRD results discussed above.

CONCLUSIONS

In this work, we produced layered WO$_3$/ReO$_3$, ReO$_3$/WO$_3$ and mixed ReO$_3$–WO$_3$ thin films by reactive DC magnetron sputtering and subsequent annealing in air. In contrast to previously reported methods, our synthesis method benefits from high flexibility in the Re-to-W ratio in the resulting material, allowing high Re content (>50%) at moderate temperatures and without the use of high pressure. The possibility to vary Re content over a wide range opens a route for tweaking and fine tuning the properties of ReO$_3$–WO$_3$ to meet the needs of potential applications.

Separate cubic ReO$_3$ (Pm3m) and monoclinic WO$_3$ (P2$_1$/n) phases were found by Rietveld refinement of XRD patterns in layered thin films; WO$_3$/ReO$_3$ (sample #3) and ReO$_3$/WO$_3$ (sample #4) were annealed at 450 °C. However, the tetragonal (P4/nmm) phase was found in layered ReO$_3$/WO$_3$ (sample #5) and mixed ReO$_3$–WO$_3$ films (samples #6, #7, #8), which possibly indicates the formation of Re$_{1-x}$W$_x$O$_3$ solid solutions. Conductive AFM measurements confirm rhenium oxide diffusion through the WO$_3$ layer during annealing (samples #4 and #5). Macroscopic electrical measurements and conductive AFM show correlation of film conductivity with the increase of Re content in mixed ReO$_3$–WO$_3$ thin films.

First-principles DFT calculations were performed for selected compositions of Re$_{1-x}$W$_x$O$_3$ solid solutions to predict their crystallographic phase and electronic properties. The calculations suggest that Re$_{1-x}$W$_x$O$_3$ solid solutions possess electrical
Figure 10. Total and projected densities of states (DOSs) of the set of atomic orbitals for the four selected models of Re$_x$W$_{1-x}$O$_3$ solid solutions and pure ReO$_3$ for comparison. The energy zero is set at the Fermi level $E_F$. The supercells used in the calculations are shown at the bottom, and lattice parameters are shown for each model.
conductivity, which was confirmed by microscopic and macroscopic electrical measurements. Moreover, our DFT calculations predict that the addition of tungsten to ReO$_3$ induces tetragonal distortion of the lattice in agreement with the XRD results. The new synthesis method of crystalline layered ReO$_3$ /WO$_3$ and mixed ReO$_3$–WO$_3$ thin films opens the door for further studies.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05085.

Detailed description of sample characterization, first-principles DFT calculations and data, visual appearance of the samples, transmittance spectrum of the pure ReO$_3$ thin film, TEM images, high-magnification AFM images, and high-magnification SEM images (PDF)

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**Notes**

The authors declare no competing financial interest.

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