Phase behaviour of 2D MnWO$_x$ and FeWO$_x$ ternary oxide layers on Pd(1 0 0)

N Doudin, D Kuhness, M Blatnik, F P Netzer and S Surnev

Surface and Interface Physics, Institute of Physics, Karl-Franzens University Graz, Universitätsplatz 5, 8010 Graz, Austria

E-mail: svetlozar.surnev@uni-graz.at

Received 28 March 2017
Accepted for publication 25 April 2017
Published 12 May 2017

Abstract
The structure and properties of ternary oxide materials at the nanoscale are poorly explored both on experimental and theoretical levels. With this work we demonstrate the successful on-surface synthesis of two-dimensional (2D) ternary oxide, MnWO$_x$ and FeWO$_x$, nanolayers on a Pd(1 0 0) surface and the understanding of their new structure and phase behaviour with the help of state-of-art surface structure and spectroscopy techniques. We find that the 2D MnWO$_x$ and FeWO$_x$ phases, prepared under identical thermodynamic conditions, exhibit similar structural properties, reflecting the similarity of the bulk MnWO$_4$ and FeWO$_4$ phases with the wolframite structure. Structure models of prototypical 2D ternary oxide phases are proposed and discussed in the light of new structure architecture concepts which have no analogues in the bulk.

Keywords: 2D oxides, ternary oxides, metal tungstates, palladium, scanning tunnelling microscopy, x-ray photoelectron spectroscopy

(Some figures may appear in colour only in the online journal)

1. Introduction

Metal tungstates, with the general formula MWO$_4$ (M denotes a bivalent metal cation), have been intensively studied due to their high application potential in various fields, such as in photoluminescence [1], microwave devices [2], photoanodes [3, 4], electrochromic systems [5], scintillation materials [6], humidity sensors [7], magnetic properties [8, 9] and catalysis [10, 11]. In particular, the two end members of the natural wolframite minerals (Fe$_x$Mn$_{1-x}$WO$_4$) huebnerite (MnWO$_4$) and ferberite (FeWO$_4$), are semiconductors with a band gap between 2.1 and 2.3 eV [12], i.e. in the visible light range, which makes these materials attractive for ‘green’ technology applications in photoanodes for photocatalytic water splitting to produce hydrogen [4] and energy efficient electrochromic smart windows [5]. Because the 3d shell is incomplete, transition metal tungstates undergo phase transition from paramagnetic (at 300 K) to antiferromagnetically ordered states at low temperatures [13, 14]. In particular, MnWO$_4$ is a prototypical magnetoelectric multiferroic, in which the spiral spin structure and the ferroelectric polarization simultaneously appear [15], and it is thus a promising material for the design of novel spintronic devices, such as tunnel magnetoresistance sensors and spin valves with electric field tunable functions.

The physical and chemical properties of metal tungstates at the two-dimensional (2D) limit are poorly understood. Recently, we have fabricated 2D CuWO$_4$ [16] and FeWO$_3$ [17] nanolayers via a physical vapor deposition approach, using the solid state chemical reaction of a (WO$_3$)$_2$ cluster beam from the gas phase with well-ordered (2 x 1)-CuO and FeO(1 1 1) monolayer phases on Cu(1 1 0) and Pt(1 1 1) surfaces, respectively. The complex structure of these 2D tungstate phases has been interpreted with the help of density functional theory (DFT) calculations and consists of new building elements with no bulk analogs. As a consequence, they may display unusual physical properties, such as the ferromagnetic ground state theoretically predicted for the FeWO$_3$ layer [17], in contrast to the antiferromagnetic behavior of the bulk FeWO$_4$ phase.

In this article, we extend the palette of 2D tungstate phases to include various MnWO$_x$ and FeWO$_x$ nanostructures grown onto a Pd(1 0 0) surface, and determine their atomic structure and stoichiometry with surface science techniques, including scanning tunnelling microscopy (STM), x-ray photoelectron spectroscopy (XPS) and high-resolution electron energy loss
spectroscopy (HREELS). The choice of the Pd(1 0 0) substrate has been motivated by the fact that the growth mechanism and structure of the constituent 2D binary MnO2 [18, 19], FeO, [20], and WO3 [21] phases on Pd(1 0 0) is well established. We have fabricated 2D MnWO4 and FeWO4 ternary oxide layers by utilizing the solid-state chemical reaction between the binary MnO2 (FeO2) and WO3 phases on the Pd(1 0 0) surface. The 2D MnWO4 and FeWO4 layers are found to display a rich phase behavior as a function of the oxygen chemical potential: from an oxygen-rich layered hexagonal phase, weakly coupled to the substrate, to oxygen-poor bilayer commensurate structures. Generally, the 2D Mn- and FeWO4 layers, generated under equivalent preparation conditions, display similar structural properties to each other, reflecting the structural similarity of their bulk counterparts (MnWO4 and FeWO4), crystallizing with the wolframite structure. Specifically, some structural differences between these phases have been encountered, which have been attributed to the different alloying behaviour of Mn and Fe atoms with the Pd(1 0 0) substrate. Tentative structure models are proposed, with building assemblies that have no correspondence in the respective bulk compounds.

2. Experimental

STM measurements have been performed in two ultra-high vacuum (UHV) systems (base pressures ~1 × 10−10 mbar), equipped with variable-temperature STM’s (Oxford Instruments and Omicron), LEED and facilities for sample manipulation, cleaning and physical vapour deposition, as described elsewhere [22, 23]. Both STM instruments were operated at room temperature in constant current mode using electrochemically etched tungsten tips. XPS experiments have been carried out mainly in our home laboratory, in a UHV chamber equipped with a dual x-ray source for Mg Kα and Al Kα radiation and a hemispherical electron analyzer (PHOIBOS 100, SPECS). Typically, Mg Kα radiation has been used to excite W 4f, Mn 2p, Fe 2p, Pd 3d core-level and O KLL Auger electron spectra. Some XPS measurements have been also performed with high spectral resolution at beamline I1311 in the Swedish synchrotron radiation laboratory MAX-Lab, Lund, Sweden. A Shirley background was subtracted from all core level spectra. The W 4f core-level spectra have been decomposed into several components, whose individual shape consists of a Donjach-Sunjic profile convoluted with a Gaussian distribution [24]. HREELS experiments have been conducted in a UHV system equipped with a high-resolution electron energy loss spectrometer (Delta 0.5, SPECS) capable of a total energy resolution of ~1 meV, which was operated in specular reflection geometry at 60° incidence from the surface normal and with a primary energy of 4.0 eV. The Pd(1 0 0) surface has been cleaned by cycles of Ar ion sputtering (1.5 keV) and annealing to 1000 K. Mn and Fe atoms have been evaporated from commercial electron beam evaporators, while a beam of (WO3)3 clusters has been generated by thermal sublimation of WO3 powder at 1300 K in a thermal evaporator [16]. The Mn, Fe and WO3 deposition rates have been controlled by a quartz microbalance. The 2D MnWO4 and FeWO3 ternary oxide layers on Pd(1 0 0) have been fabricated by using two different preparation approaches. In the first one, Mn- or Fe-oxide nanolayers with well-defined structure, such as hexagonal MnO2 trilayer [18, 19] or c(8 × 2)-FeO bilayer [20], have been grown first on the Pd(1 0 0) surface. For this purpose, one monolayer (ML) of Mn or Fe metal has been reactively evaporated in oxygen atmosphere onto the clean Pd surface to form the desired binary oxide structures (1 ML is defined by the density of the surface atoms of the Pd(100) surface, i.e. 1.32 × 1015 atoms·cm−2). Subsequently, 0.5 ML of (WO3)3 clusters has been deposited at 300 K onto the MnO2 or FeO layers. In a final step, the mixed oxide film has been subjected to annealing at elevated temperatures in oxygen atmosphere (with an O2 pressure of up to 5 × 10−6 mbar) or in UHV to initiate the solid-state reaction between the binary MnO2 (or FeO) and (WO3)3 layers, generating the ternary MnWO4 (or FeWO4) phases. In the second approach, the preparation procedure is reversed and involves first the deposition of 0.5 ML (WO3)3 clusters directly onto the Pd(1 0 0) surface to form a well-ordered 2D WO3 layer with a c(2 × 2) structure [21]. This is then followed by deposition of 1 ML Mn or Fe atoms and annealing in oxygen or UHV. Both preparation routes were found to lead to similar results, with the first one yielding better structural order in the MnWO4 layers, and the second one in the FeWO4 layers.

3. Results

3.1. Morphology and surface structure

Under the most oxidative conditions employed in this work, e.g. annealing the MnWO4 and FeWO4 films in O2 atmosphere with a pressure of 5 × 10−6 mbar and temperatures between 673 K and 823 K (typically, lower annealing temperatures were used for the FeWO4 layers), phases with hexagonal symmetry and identical lattice parameters form, named hereafter HEX for brevity. Figure 1 reveals details on the HEX MnWO4 structure on Pd(1 0 0), as derived by STM and LEED, which are also representative for the HEX FeWO4 layers [25]. The large-scale STM image in figure 1(a) shows that the HEX phase forms a 2D wetting layer which almost fully covers the Pd(1 0 0) surface, with only few patches of dark contrast visible, corresponding to bare Pd areas. The latter serve as a reference for estimating the apparent height of the HEX layer with respect to the Pd(1 0 0) surface, which measures 3.6 ± 0.2 Å. The 2D HEX layer consists of domains, which display in STM stripes running parallel to the two principal substrate directions [0 1 1], and [0 1 1]. The domains with the stripes oriented nearly perpendicular to the fast scanning (horizontal) direction (indicated A) appear somewhat brighter that the domains with the nearly horizontal stripes (indicated B).

The STM image in figure 1(b) shows that the A- and B-type domains correspond to two equivalent rotational (90°) domains of the oxide film, which exhibit a hexagonal structure. The latter is clearly recognized in the high-resolution STM image in figure 1(c) of domain A, which displays a hexagonal arrangement of protrusions (unit cell indicated with a black line) with a lattice constant of 6.1 ± 0.1 Å. This is in
line with the experimental LEED pattern in figure 1(d), which shows two rings, each consisting of 12 diffraction spots, arising from the two orthogonal domains with the hexagonal structure. One lattice vector of the HEX overlayer is aligned either with the \([0 1 1]\) (domain A) or the \([0 1 1]\) (domain B) substrate directions. A line profile taken along such an atomic row (white line in figure 1(b)) is plotted in the inset of figure 1(b) and reveals that the atomic corrugation is modulated by a long wavelength with a periodicity of \(30.5 \pm 0.2 \text{ Å}\), due to the stripes. Within this periodicity there are exactly 5 maxima separated by the lattice spacing \(a_{\text{HEX}}\) of the HEX phase, which indicates that the stripe pattern is the result of a Moiré-effect between the oxide overlayer and the Pd substrate. Indeed, \(5a_{\text{HEX}} \approx 11a_{\text{Pd}} = 30.25 \text{ Å}\), which is in perfect agreement with the measured stripe periodicity. This finding is exemplified in the lattice model of figure 1(e), where the lattice parameter of the HEX phase was adjusted to \(6.05 \text{ Å}\) to fit the above lattice coincidence condition. The calculated LEED pattern with this model is shown in figure 1(f) and reproduces fully the experimental one.

Annealing the MnWO₃-HEX layer in UHV at 873 K causes no visible changes in the STM images, which as before display the coexistence of the orthogonal domains A and B (figure 2(a)). However, the LEED pattern (figure 2(b)) has changed significantly and shows series of diffraction spots parallel to the main substrate directions. The Fourier transform (figure 2(c)) of the image in figure 2(a) reproduces well the LEED pattern and reveals some small deviations from the hexagonal symmetry. These deviations are too small to be reliably detected directly from the STM images, even when taken at high resolution, as the one in figure 2(d). This image shows that 5 overlayer lattice spacings fit into the Moiré pattern periodicity of \(30.5 \text{ Å}\) along the \([0 1 1]\) (horizontal) direction as before, implying that the lattice vector length in this direction remains unaltered. Consequently, the length of the second lattice vector and/or the angle between the two vectors must have changed in the new structure. We have tested different configurations by varying the length and the angle of the second lattice vector and have generated the corresponding LEED patterns. The overlayer lattice model showing the most reasonable agreement between the calculated (figure 2(f)) and experimental LEED is shown in figure 2(e) and can be described with the matrix \(M = \begin{pmatrix} 2.2 & 0 \\ -1 & 2 \end{pmatrix}\). Here, the tip of the second lattice vector with a length of \(6.15 \text{ Å}\) (i.e. by \(1.6\%\) longer than in the HEX phase) is coinciding with a lattice point in every second row and the angle between the two lattice vectors is now \(117^\circ\). Due to these small deviations from the ideal hexagonal structure, this new phase was named \textit{distorted} HEX. We note parenthetically that similar distorted structures have been encountered also for the binary MnOₓ layers on Pd(100) \([18, 19]\), which has been attributed to their high structural flexibility. The apparent height of the MnWO₃ \textit{distorted} HEX layer with respect to the Pd(100) surface measures 2.5 Å, i.e. it is thinner than the HEX layer (3.6 Å). The reduced thickness implies that the oxide film is stronger interfacially coupled to the Pd substrate, which is probably the reason for the row matching condition in the model of figure 2(e).
Turning now to the FeWO$_x$-HEX layer, annealing at a temperature of 873 K in 5 \times 10^{-6} \text{ mbar} \text{ O}_2 (i.e. under more reducing thermodynamic conditions) generates a new oxide phase with an oblique unit cell (named hereafter in short OBL). Figure 3(a) shows that this phase also forms a 2D layer on the Pd(100) surface, which exhibits a stripe pattern with a periodicity of ~28 Å, oriented parallel to the main substrate directions. The high-resolution STM image in figure 3(b) displays the oblique lattice surface (unit cell drawn in the image) with unit cell vectors $a = 5.6 \pm 0.1$ Å and $b = 4.4 \pm 0.1$ Å, crossing at an angle of 95°, which are not aligned with any of the substrate high symmetry directions. The image reveals also that the stripe (Moiré) pattern in figure 3(a) is due to the height modulations caused by the coincidence registry of the FeWO$_x$ layer with the Pd substrate. This is best recognized in the line profile reproduced in figure 3(c), which is taken perpendicular to the stripe direction (white line in figure 3(b)), which coincides with the direction of one of the diagonals $d_{\text{OBL}}$ of the OBL unit cell. Here, four $d_{\text{OBL}}$ fit exactly to the stripe periodicity of 28 Å, which is very close to 10$a_{\text{Pd}} = 27.5$ Å. This suggests that the OBL layer, although being incommensurate to the substrate, is rotationally aligned to the latter to achieve the best possible interfacial matching. The corresponding LEED image (figure 3(d)) contains diffraction spots arranged in a complex pattern, as expected for a low symmetry structure, which coexist with numerous spots aligned along the main substrate directions, resulting from the Moiré pattern. In figure 3(e) we propose a lattice model for the OBL phase, which takes the established rotational alignment and coincidence relationship to the Pd substrate into account. The corresponding calculated LEED image is reported in figure 3(f). Besides the 4 $d_{\text{OBL}} = 10a_{\text{Pd}}$ coincidence relation (the coincidence lattice points are encircled with a solid line), the specific rotational angle results in a row matching condition of 3 overlayer lattice constants with every 4th Pd row in the [0 1 1] (or [0 1 1]) direction (lattice points encircled with dashed lines). Indeed, weak modulations of every third overlayer row in the [0 1 1] direction can be recognised in the STM image in figure 3(b) (marked with black dashed lines). Also here, we attribute the good lattice matching between the OBL-FeWO$_x$ layer and the Pd(100) surface to lattice flexibility as a result of the reduced film thickness of 2.2 Å [26].

Eventually, under stronger reducing preparation conditions, i.e. annealing the FeWO$_x$ and MnWO$_x$ layers on Pd(100) in UHV to 823 K and 1000 K, respectively, 2D ternary oxide phases form, which exhibit an apparent height of only about 1 Å and a characteristic appearance in the STM images (figures 4(a) and (d)), resembling a rush mat pattern. The MnWO$_x$ rush mat layer displays a square structure (unit cell is indicated in figure 4(a)) with unit cell vectors of length 11.7 Å and rotated by 45° with respect to the [0 1 1] and [0 0 1] substrate directions. The corresponding LEED image (figure 4(b)) shows accordingly a square diffraction pattern, which is compatible with a commensurate $3(\sqrt{2} \times \sqrt{2})R45^\circ$ structure (see a lattice model in figure 4(c)). Interestingly, the FeWO$_x$ rush mat phase, although displaying very similar structure motifs in the STM image (figure 4(d)), has slightly different lattice parameters. The unit cell (indicated in figure 4(d)) is not square, but
Figure 3. The 2D OBL-FeWO<sub>x</sub> phase on Pd(1 0 0): (a) large STM image (100 × 100 nm<sup>2</sup>, 2.0 V, 100 pA); (b) high-resolution STM image (8 × 8 nm<sup>2</sup>, 0.05 V, 2.0 nA) of the OBL layer with the unit cell indicated. The black dashed lines mark rows in registry with the substrate; (c) line profile taken along the white line in (b); (d) LEED pattern (E = 50 V), (e) lattice model, and calculated LEED image (f) of the OBL phase.

Figure 4. The 2D rush mat phases on Pd(1 0 0): (a) high-resolution STM image (7 × 7 nm<sup>2</sup>, 0.3 V, 300 pA) of the rush mat MnWO<sub>x</sub> layer with the unit cell indicated; (b) corresponding LEED pattern (135 V) and (c) lattice model; (d) high-resolution STM image (5 × 5 nm<sup>2</sup>, 0.5 V, 500 pA) of the rush mat FeWO<sub>x</sub> layer with the unit cell indicated; (e) corresponding LEED pattern (50 V) and (f) lattice model.
quasi-rhombic: one of the unit cell vectors with a length of 11.0 Å is aligned in the [0 1 1] direction, the second vector is slightly longer, 11.3 Å, and is rotated by ~77° with respect to the first one. The corresponding LEED pattern (figure 4(e)) has been analysed in detail in [26]. It was found that most of the diffraction spots can be generated from a commensurate lattice model, shown in figure 4(f), which is described in the matrix notation by the matrix: \[ M = \begin{pmatrix} 4 & 0 \\ 1 & 4 \end{pmatrix}. \]

3.2. Spectroscopic characterization: XPS and HREELS

Figure 5 summarizes W 4f, Mn 2p3/2, Fe 2p3/2 core level spectra and O KLL Auger electron spectra (the latter were collected instead of the O 1s spectra, which overlap strongly with the Pd 3p substrate peak) of the MnWO4, (top panels) and FeWO4 (bottom panels) phases. To recall, the HEX MnWO4 layer has been prepared by deposition of (WO3)3 clusters onto a hexagonally ordered MnO2(1 1 1) trilayer on Pd(100), followed by an oxidation in 3 × 10⁻⁶ mbar O2 at 823 K [25]. In contrast, the isostructural HEX FeWO4 layer has been generated by reactive evaporation of Fe atoms at 300 K onto the 2D WO3/Pd(100) surface.

The W 4f spectra of the HEX MnWO4 (bottom curve in figure 5(a)) and HEX FeWO4 (bottom curve in figure 5(d)) show, as expected from their identical structure, similar line shapes consisting of a broad 4f7/2-4f5/2 doublet, separated by a spin-orbit splitting of 2.1 eV. Both spectra have been decomposed into two different doublet components with binding energies (BE) of 35.1 eV (blue curve) and 35.7 eV (red curve) and of almost equal intensities, which correspond formally to W⁵⁺ and W⁶⁺ species, respectively, in bulk tungsten oxide compounds [27]. The corresponding Mn 2p3/2 spectrum (middle curve in figure 5(b)) exhibits the same peak position (641.0 eV) and a similar line shape (albeit somewhat broadened) as that of the MnO2(1 1 1) trilayer (bottom curve in figure 5(b)), which implies that the Mn atoms in the HEX-MnWO4 layer retain their octahedral oxygen coordination, as in the MnO2 phase. The integrated intensity of the Mn 2p signal in the HEX-MnWO4 phase is attenuated by ~25% with respect to that of the pristine MnO2 layer, suggesting that the Mn atoms in the
Figure 6. (a) W 4f spectra of the rush-mat -FeWO₃ (top curve) and 3(√2 × √2)R45°-MnWO₃ layers (bottom curve). The W 4f spectra are excited with a photon energy of 140 eV; The bottom curves in (b) and (c) show their corresponding Mn 2p₃/₂ and Fe 2p₃/₂ spectra. The spectra of the dist. HEX and OBL phases (top curves) are also shown here for comparison. The Mn 2p₃/₂ spectra have been excited with a photon energy of 800 eV, the Fe 2p₃/₂ spectra with a laboratory Mg Kα radiation source.

The HEX layer are located in deeper positions under the surface. This is corroborated by the angular dependent XPS measurements summarized in figure 5(c), which show the relative changes in the W 4f, Mn 2p and Pd 3d intensities in moving from normal emission (θ = 0°) to the more surface sensitive grazing emission angle of 60°. Indeed, the increase (decrease) of the W 4f (Mn 2p) signals with the emission angle is a clear evidence that the W atoms are located close the HEX-MnWO₃ surface, whereas the Mn atoms are buried near the metal-oxide interface. The W atoms are highly oxidized (with oxidation states of 5+ and 6+), which implies that the oxide surface is oxygen terminated. From the attenuation of the Pd 3d substrate intensity the thickness of the HEX layer is estimated to be ~4 Å [25], which is in good agreement with the apparent height of 3.6 Å, derived from the STM images.

For the HEX-FeWO₃ layer, similar results are obtained from the Fe 2p₃/₂ spectra presented in figure 5(e). After the reactive deposition of 1 ML Fe in 2 × 10⁻⁷ mbar O₂ at 300 K, a disordered layer with a FeO stoichiometry forms on the WO₃/Pd(100) surface. This is evidenced by the bottom Fe 2p₃/₂ spectrum in figure 5(e), which exhibits a peak maximum at 709.5 eV and a satellite structure (indicated Sat.) at a 6eV higher BE, both typical for Fe²⁺ species [28]. The post-oxidation annealing step in 5 × 10⁻⁶ mbar O₂ at 673 K initiates the FeO/WO₃ layers to form the HEX-FeWO₃ phase, for which the Fe 2p₃/₂ peak maximum (middle spectrum in figure 5(e)) is shifted to a higher BE of 710.3 eV, characteristic of Fe³⁺ species [28]. This phase is indeed oxygen enriched, as inferred from the corresponding O KLL Auger spectrum (middle curve in figure 5(f)). Similar Fe 2p core level shifts have been also reported for the oxidation of FeO(1 1 1) bi-layers, supported on Pt(1 1 1) [29] and Pd(100) [20] surfaces, to form hexagonal FeO₂ trilayers. This would suggest that the Fe atoms in the HEX-FeWO₃ phase are octahedrally coordinated to O, as in the HEX-MnWO₃ phase. Similarly, the Fe atoms are also located near the metal-oxide interface, as deduced from the reduction of the Fe 2p intensity after the post-oxidation step.

As established in the previous section, under less oxidizing conditions the HEX phase transforms into the dist. HEX (MnWO₃) and OBL (FeWO₃) 2D structures, which exhibit a reduced thickness (~2.5 Å) with respect to the HEX layers. Interestingly, both the dist. HEX and OBL phases display similar W 4f spectra (top curves in figures 5(a) and (d), respectively), which are broadened at the lower binding energy side. To account for this broadening a minor third W 4f core level component with a BE of 34.4 eV has been introduced in the peak fitting analysis, which formally corresponds to W⁴⁺ species [27]. We attribute this component to W atoms associated with surface defects, such as oxygen vacancies. This is fully in accord with the STM image of the dist. HEX phase (figure 2(d)), which shows an increased number of dark depressions, characteristic of missing O atoms on oxide surfaces [21]. The corresponding Mn 2p₃/₂ (top curve in figure 5(b)) and Fe 2p₃/₂ spectra (top curve in figure 5(e)) show also a shift of the spectral weight to lower binding energies, which are indicative of a lower oxidation state of the Mn and Fe species in the dist. HEX and OBL structures, respectively, as compared to the HEX phases (see also the decrease of the O KLL intensity in the OBL layer, top curve in figure 5(f)). The oxide reduction is accompanied by a significant loss of Mn (Fe) atoms, as revealed by the drop of the Mn 2p (Fe 2p) intensity in the dist. HEX (OBL) phase, which species tend to form surface alloys [30-33] with the Pd(100) substrate. This suggests that the reduction process starts primarily at the metal-oxide interface, followed by diffusion of Mn and Fe into the Pd bulk, which causes the observed thinning of the dist. HEX (OBL) layers.

The alloying of the Mn and Fe atoms with the Pd substrate plays further a decisive role in the formation of the 2D rush-mat MnWO₃ and FeWO₃ layers, reported in figure 4. Their similar structure is also reflected in the corresponding W 4f
spectra (figure 6(a)), which if taken at high resolution using a synchrotron light source, display a single component with a W 4f/2 BE of 33.6 eV and extremely sharp (FWHM \( \leq 0.3 \text{eV} \)) line shape. Recently, we have grown a 2D-FeWO\(_3\) layer on a Pt(111) surface, where the W and Fe atoms are in direct contact with the Pt substrate and arranged in a mixed honeycomb layer, terminated by bridging oxygen atoms [17]. The W atoms in the FeWO\(_3\) phase have a three-fold O coordination and exhibit a similar BE (33.9 eV), which may suggest an analogous building architecture of the 2D rush mat layers, as discussed in the next section. The corresponding Mn 2p/2 (bottom curve in figure 6(b)) and Fe 2p/2 (bottom curve in figure 6(c)) spectra show that the transition from dist. HEX and OBL phases (their respective spectra are presented for comparison in figures 6(b) and (c)) to the rush-mat structures is associated with a further loss of Mn and Fe species, due to their diffusion into the Pd substrate. The Mn 2p/2 spectrum of the \( 3(\sqrt{2} \times \sqrt{2})R45^\circ \) MnWO\(_3\) layer exhibits a sharp structure at a BE of 639.2 eV, which is characteristic of the formation of a well ordered Pd–Mn surface alloy on the Pd(100) surface with a \( c(2 \times 2) \) (or alternatively \( (\sqrt{2} \times \sqrt{2})R45^\circ \)) structure [32]. The latter may exert a templating effect on the structure of the MnWO\(_3\) overlayer, whose unit cell is exactly 3 times larger than that of the Pd–Mn(100) surface. For the Pd-Fe system only a disordered surface alloy with a face-centered tetragonal structure has been reported [33], which is possibly the reason for the distorted unit cell of the FeWO\(_3\) rush mat phase.

In view of the general character of the HEX ternary oxide phase, which forms not only in MnWO\(_3\) and FeWO\(_3\), but also in the NiWO\(_3\) layers on Pd(100) [25], and to gain more information on its structure, this particular phase has also been characterized with HREELS phonon spectroscopy. Figure 7 shows an HREELS spectrum of the HEX MnWO\(_3\) phase, which contains two intense loss peaks at 45 and 97 meV and weaker structures at 72, 107 and 118 meV. These phonon peaks fall in the frequency regions where stretching (75–120 meV) and bending (25–50 meV) vibrational modes of W–O–W structure elements of WO\(_3\) compounds occur [34]. This is a clear indication that the W atoms of the HEX-MnWO\(_3\) surface are terminated by bridging oxygen atoms. This is in contrast with the structure of the 2D WO\(_3\) layer on Pd(100), which is terminated by W = O (tungstyl) groups, characterized by a strong loss peak at 125 meV [21]. The phonon loss at 45 meV may also originate from the stretching vibrations of O atoms against the Mn layer [35].

4. Discussion

Based on the structure and spectroscopic analysis presented above, tentative structure models of the HEX and rush-mat layers on Pd(100) are constructed, which correspond to the most oxygen-rich and oxygen-poor ternary oxide phases obtained under the employed preparation conditions. The structure model of the HEX phase is illustrated in figure 8(a) and consists of a stack of five O–Mn(or Fe)–O–W–O layers, counted from the Pd surface. The first three layers retain the structure of the pristine O–Mn–O trilayer on Pd(100), which is hexagonal with a lattice constant of \( \approx 3.1 \text{Å} \) [18, 19]. The lattice constant of the HEX phase is \( \approx 6.1 \text{Å} \), i.e. the terminal W–O layers exhibit a kind of a \( (2 \times 2) \) superstructure. The latter can be realized with the W atoms arranged either in a honeycomb- or in a kagomé-lattice above the O–Mn–O layer, with two and three W atoms, respectively. Since the W coverage in the HEX phase is fixed to 0.5 ML, the only possible configuration for the W atoms is the honeycomb one, as shown in the top view of figure 8(a). Recently, Barcaro et al [36] have theoretically analysed the thermodynamic stability of several honeycomb configurations in a hexagonal \( (2 \times 2) \) unit cell, and we make here use of their results. Considering only high-symmetry threefold hollow or on-top sites for the W atoms, two honeycomb adsorption geometries are possible: (i) the W atoms sit in alternating fcc and hcp sites of the O layer, and (ii) one W atom sits in a fcc position and the second one is located on-top of one O atom. The former adsorption geometry would generate two quasi-equivalent W atoms with octahedral oxygen coordination (considering also the terminating O layer), thus both in the maximal oxidation state 6+. This model is definitely incompatible with the STM and XPS results of the HEX phase: it would generate a honeycomb surface lattice in STM and a single W 4f component in XPS, which are not observed experimentally. The second geometry (shown in the model in figure 8(a)) results in two inequivalent W species, with octahedral (coloured dark blue) and tetrahedral O coordination (coloured light blue).
The latter is favoured by the experimental data: only one W species is imaged bright in STM and two W 4f components are present, corresponding to W oxidation states of 6+ and 5+ (the W atom sitting on-top is likely coordinated via a short W–O bond to the underlying O atom). The W atoms are linked by oxygen atoms, which form the O termination layer. The formal stoichiometry of the HEX layer is thus O₄–Mn₄–O₄–W₂–O₃, or Mn₄W₂O₁₁, which is not observed in the bulk phase. This may be due partly to its polar character, so this hexagonal tungstate structure can be stabilized only in 2D form on a metal surface. Stoichiometrically, the HEX phase lies very close to the bulk Fe₂WO₆ phase, which forms upon the oxidation of ferberite (FeWO₄) [37], with the Fe atoms changing their oxidation state from 2+ to 3+. Structurally, the HEX layer shows some resemblance to the bulk MnWO₄ (or FeWO₄) structure, which consists of a similar stacking layer sequence along the [1 0 0] direction, but only the O layers exhibit a quasi-hexagonal structure, whereas the Mn(Fe) and W layers display a rectangular lattice.

Figure 8(b) shows a model of the rush-mat phase for the 3(√2 × √2)R45° MnWO₃ layer. It was constructed by linking triangular MnWO₃ building elements (indicated with black dashed line) to form the 3(√2 × √2)R45° unit cell. Indeed, similar triangular-shaped protrusions can be recognized in the STM images in figure 4. Triangular FeWO₃ units have been predicted in DFT calculations to be the ingredients of the honeycomb (2 × 2)-FeWO₃ and (6 × 6)-Fe₆W₈O₂₁ phases on Pt(111) [17]. The rush-mat phase thus corresponds to a mixed Mn(Fe)-W layer, in direct contact with the Pd(100) surface, which is terminated by a layer of O atoms sitting in bridging positions between the metal atoms. The overall film stoichiometry is MnWO₃ (or FeWO₃), i.e. identical to that of the (2 × 2)-FeWO₃ layer on Pt(1 1 1). The reduced number of Mn(Fe) and W atoms in the rush mat structure with respect to the HEX phase is in line with the experimentally observed loss of Mn(Fe) and W atoms: the former species diffuse into the Pd bulk, whereas W partially desorbs as WOₓ during the reductive annealing.

5. Conclusions

We have investigated the phase behaviour of 2D ternary oxide MnWOₓ and FeWOₓ nanolayers grown epitaxially on a Pd(100) surface. Their structure and composition vary strongly with the oxygen chemical potential: from an oxygen-rich layered hexagonal phase, weakly coupled to the substrate, to oxygen-poor bilayer commensurate structures, strongly bound to a Pd–Mn(Fe) alloyed interface. For these two extremes, structure models have been suggested, with building principles that have little in common with the corresponding bulk compounds. This is due, on the one hand, to the stabilization of polar structures at the nanoscale, and on the other hand, to the interaction with the metal substrate. Our study underlines the importance of the multi-technique characterization, combined with a precise control of the amount of metal and oxygen atoms involved, for unravelling the structure and stoichiometry of 2D ternary oxide layers.

Acknowledgments

This work has been financially supported by the FWF Project P26633-N20.
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