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The Ultrathin WO Bilayer on a Ag(100) Surface: A Model for the Structure of 2D WO Nanosheets

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Figure 1

Figure 2

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Figure 8

Figure 9

**The Ultrathin WO₃ Bilayer on Ag(100):
A Model for the Structure of 2D WO₃ Nanosheets**

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ABSTRACT

Two-dimensional (2D) WO_3 nanosheets exhibit a range of novel properties and functionalities that render them attractive for advanced nanotechnologies. However, at the ultimate 2D limit of single – layer thickness the structural properties of WO_3 are unclear. Here we fabricated, using MBE techniques, a crystalline 2D WO_3 overlayer on a $\text{Ag}(100)$ surface and unveil its geometric, electronic and vibrational structure via a combination of state-of-the-art experimental (microscopic and spectroscopic) and computational techniques. The 2D WO_3 phase forms a bilayer with staggered arrangement of WO_6 octahedra, linked together by corner and edge sharing, which is significantly different from the cubic and monoclinic WO_3 bulk structures, but resembles a bilayer of the $\alpha\text{-MoO}_3$ layered bulk lattice. Such 2D WO_3 bilayer on $\text{Ag}(100)$ is a robust non-polar structure, which is incommensurate in various rotational orientations, weakly coupled to the metal substrate, and according to the density functional theory (DFT) calculations should survive as a stable free-standing layer, i.e. as a nanosheet.

1. INTRODUCTION

Two-dimensional (2D) nanosheets, consisting of one to few atomic layers and displaying extended scale planar dimensions, are considered as building blocks for assembling multifunctional materials with well-defined architectures.¹ The thickness confinement at the atomic scale and the large surface – to – volume ratio may induce a wide range of unique electronic, magnetic and optical properties, which makes the 2D nanosheets promising candidates for the fabrication of next-generation nano-electronic or -optical devices. Nanosheets are typically prepared in the form of individual host layers by exfoliation from bulk materials with a layered structure.² Various delamination techniques have been developed for generating 2D flakes of graphene,^{3,4} boron nitride,^{2,5} metal disulfides^{2,6} and some metal oxides,⁷ where the propensity for exfoliation is facilitated by the weak van-der-Waals interlayer interactions and strong in-plane atomic bonds in the host layered compound. Due to the 2D confinement most of the atoms make up the surfaces of the nanosheet, and as a consequence significant lattice distortions and bond rearrangements may occur with respect to the ideal structure of their parent bulk compounds. This tendency is particularly pronounced in materials, for which no layered structures are stable in the bulk, such as titania,⁸⁻¹⁰ ZnO¹¹ and WO₃.¹² For instance, density-functional theory (DFT) calculations of rutile TiO₂(001) have predicted that below a critical thickness, layered TiO₂ structures become energetically more favourable,⁸ which facilitates their delamination into monolayer titania sheets.^{9,13} In addition, the latter display small distortions of the TiO₆ octahedra, resulting in a strongly modified angular nanosheet self-assembly.⁹

Tungsten trioxide, WO₃, is a material of special interest because of its rich phase diagram and attractive properties for various applications in catalysis,¹⁴⁻¹⁷ electrochromic devices,^{18,19} chemical sensors²⁰ and photo-electrochemical water splitting.²¹⁻²⁴ The crystal structure of WO₃ is based on the cubic ReO₃ lattice and consists of regular corner-sharing WO₆ octahedra, as

shown in Figure 1a for the idealized cubic WO_3 structure (lattice parameter $a = 3.77 \text{ \AA}$).²⁵ The most common and stable (between 290 K and 600 K) WO_3 polymorph is however the monoclinic $\gamma\text{-WO}_3$ phase (Figure 1b), where the WO_6 octahedra are slightly distorted and tilted, and consequently the lattice parameters are essentially twice those of the cubic WO_3 structure. 2D WO_3 materials in the form of nanosheets, nanolamellas, or nanoplates and a thickness between 1 and 100 nm have been synthesized using different preparation techniques, including hydro – and solvothermal methods,²⁶⁻²⁸ plasma treatment,^{29,30} exfoliation,^{31,32} acid etching³³ and anodization³⁴ – the current progress in this field has been summarized in a recent review paper.³⁵ WO_3 nanosheets are shown to possess a great potential in electrochromic applications, where the 2D confinement significantly increases the interfacial contact area and the charge transfer, resulting in faster color – switching speed and higher coloration efficiency.³⁶ Moreover, due to the promotion of charge carrier separation at the nanosheet junction, a remarkable photocatalytic activity has been achieved in WO_3 nanosheets, which is of one order of magnitude higher than in bulk WO_3 powders.^{28,32,37}

Figure 1. Structure models of the bulk (a) cubic WO_3 and (b) monoclinic $\gamma\text{-WO}_3$ structures. The blue and red spheres correspond to the W and O atoms, respectively. The dashed line in (a) is along the $\text{WO}_3(001)$ plane. (c) DFT-derived structure model of the $c(2 \times 2)$ WO_3 monolayer on a $\text{Pd}(100)$ surface (adapted from Ref. 38). The gray spheres correspond to the Pd atoms.

To exploit the full potential of novel physical and chemical functionalities associated with the reduced thickness in the nanoscale and to optimize the performance of WO_3 nanosheets in different applications, their geometrical structure at the 2D limit needs to be rationalized. It is generally assumed that the monoclinic $\gamma\text{-WO}_3$ structure is maintained down to the nanoscale, and that the WO_3 nanosheets typically expose the (001) planes.²⁶ Ultrathin $\text{WO}_3(001)$ nanosheets, with a thickness between 2 and 5 nm, have been recently synthesized.¹² It has been reported that DFT calculations reveal only subtle W – O bond distortions with respect to the bulk monoclinic structure (no structure details have been provided though), accompanied by a modified electron charge distribution, which is proposed to lead to a reduced chemical state of the W atoms, as observed in W 4f XPS spectra.¹² The latter have been decomposed into various core-level components, however their spectroscopic assignment is inconsistent with known W 4f binding energy values and is therefore questionable. The nature of the structural modifications occurring in 2D WO_3 nanosheets is thus not well understood.

We have recently prepared an ordered $c(2 \times 2) - \text{WO}_3$ monolayer phase on a Pd(100) single crystal surface, using the deposition of molecular cyclic $(\text{WO}_3)_3$ clusters from the gas phase.³⁸ The DFT – derived model of the $c(2 \times 2)$ structure is displayed in Figure 1c and comprises a 2D sheet cut out of the cubic WO_3 crystal parallel to the (001) plane (indicated with a dashed line in Figure 1a). It consists of corner-shared square WO_4 units, terminated by W=O tungstyl bonds at the surface; the overall stoichiometry of this oxide monolayer is WO_3 . The WO_3 monolayer is strongly bound to the Pd(100) substrate via the interfacial O atoms, and is thus under a tensile strain of $\sim 2.8\%$ which is relieved by the formation of a regular nanoscale network of antiphase domain boundaries.³⁸ Due to the relatively strong oxide-support coupling the WO_3 monolayer on Pd(100) is however not a particularly appropriate system for modelling the structural properties of WO_3 nanosheets.

In the present work, we report the fabrication of a fully stoichiometric and epitaxially ordered 2D WO₃ layer supported on a Ag(100) surface by a molecular beam epitaxy (MBE) approach and the comprehensive characterization of its novel geometric, electronic and vibrational structure using state-of-the-art surface science techniques, such as scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), high-resolution x-ray and ultraviolet photoelectron spectroscopy (XPS, UPS) using synchrotron radiation and high-resolution electron energy electron loss spectroscopy (HREELS): the experimental results have been combined with extensive first-principles DFT calculations. Despite the large lattice mismatch between WO₃ and Ag(100) (~ 7.6%) the 2D WO₃ layer grows in crystalline form as micrometer-large and rotationally-disordered domains on the Ag(100) surface: it is weakly coupled to the substrate and thus resembles a „free-standing“ 2D oxide layer. Its atomic structure has been resolved by the DFT analysis and is based on a bilayer sheet, consisting of two interleaved planes of corner – sharing WO₆ octahedra, with the octahedra of two adjacent planes sharing edges. This bilayer is fully consistent with the experimental results of XPS, HREELS and the quantitative evolution of the WO₃ coverage during growth. The stacking of WO₆ units in the WO₃ bilayer on Ag is significantly different from that in the monoclinic γ -WO₃ bulk phase: it rather resembles that of the α -MoO₃ layered structure, where such bilayers are linked only by weak van – der – Waals interactions. The here proposed WO₃ bilayer geometry is a robust structure, whereas other 2D WO₃ geometries of cubic or monoclinic origin are shown to be much less stable in the DFT simulations. We argue that such 2D WO₃ system due to its weak oxide – metal interactions is a general model of the geometry of 2D WO₃ nanosheets.

2. METHODS

2.1. Experimental

STM/LEED, high-resolution XPS, work function and HREELS experiments were performed in four different ultrahigh vacuum (UHV) chambers, described in more detail in Ref. 38. STM images were acquired at room temperature in constant current mode, with the bias applied to the sample, hence positive voltages correspond to electrons tunneling to the tip. High-resolution W 4f and O 1s photoemission spectra were measured at beamline I311 in the Swedish synchrotron radiation laboratory MAX-Lab, Lund, Sweden.³⁹ The W 4f core level spectra were decomposed into several components,⁴⁰ whose individual shape consists of a Donjach-Šunjić profile convoluted with a Gaussian distribution.⁴¹ HREELS and EELS measurements experiments were conducted with electron primary energies of 4 eV and 26 eV, respectively, and corresponding instrumental resolutions of 3-4 meV and 25 meV.

The Ag(100) surface was cleaned by cycles of Ar ion sputtering (1.5 keV) and annealing to 850 K. Surface order and cleanliness were monitored by LEED, STM and AES and XPS. The W oxide overlayer was prepared by the deposition of (WO₃)₃ clusters in UHV onto the clean Ag(100) crystal surface kept at 773 K. At this temperature, the deposited clusters condense at the surface into a compact oxide layer. The (WO₃)₃ cluster beam was generated in all UHV chambers by thermal sublimation of WO₃ powder at ~ 1250 K in a thermal evaporator; the evaporation flux was monitored by a quartz microbalance. The evaporated amount of (WO₃)₃ is given in monolayers (ML), whereby 1 ML is defined here by the density of the cubic - WO₃ (001) surface plane with a lattice constant of 3.73 Å (i.e. 7.19x10¹⁴ atoms.cm⁻²). To ensure identical oxide films in the different chambers, the WO₃ film structure was confirmed in each system by LEED.

2.2. Density-functional theory calculations

The theoretical simulations were done at the density-functional theory (DFT) level using the Quantum Espresso plane-wave package^{42,43} and the ultrasoft GBRV pseudopotentials.⁴⁴ The PBE exchange-correlation functional⁴⁵ was adopted, adding a Hubbard correction of 6 eV for the d orbitals of W (that was calibrated to give the experimental formation enthalpy of the reaction $2\text{WO}_2 + \text{O}_2 \rightarrow 2\text{WO}_3$ ⁴⁶, and used previously in Ref. 38) and Grimme-D3 empirical van der Waals corrections.⁴⁷ The methodology used in this work consists in building and optimizing different models taking into account the experimental results that revealed that the WO_3 layer has a well ordered square pattern, a thickness of about 6 Å, which corresponds to 2 full WO_3 layers, and that it also weakly interacts with the Ag substrate, having rotationally-disordered domains. Given these conditions, no defects, such as Ag insertion in the WO_3 film or different stoichiometries are considered in our models. Since the growth is incommensurate with a lattice mismatch of 7.6%, we have used a square $4 \times 4 \times 1$ Ag(100) supercell with dimensions of $11.58 \text{ Å} \times 11.58 \text{ Å}$, that applies an artificial strain of +2.7% in the 3×3 WO_3 bilayer, given that its optimized lattice parameter in a free-standing configuration at the DFT level is 3.76 Å . The Ag slab was 4 layers thick, with the bottom 2 layers kept frozen at their bulk positions, and 15 Å of vacuum in the perpendicular direction in order to avoid spurious interactions between replicated cells. The reciprocal space was sampled with a $4 \times 4 \times 1$ Monkhorst-Pack grid centered at the Γ point. The lattice parameters adopted and reported for all free standing and supported structures were the DFT optimized ones. For the evaluation of the work function, a dipole correction in the perpendicular direction was applied,⁴⁸ and the vacuum space separating replicated slabs was increased to 25 Å . Within our calculation approach the energy gap of the monoclinic bulk WO_3 structure was predicted to be 1.8 eV, i.e. by $\sim 1 \text{ eV}$ lower than the experimental value, which is in keeping with the known tendency of the PBE xc-functional to underestimate band gaps. We note that gap underestimation can in fact be corrected by applying

a Hubbard correction to both d/p states of W/O, respectively, as done recently in a work by Bondarenko et. al.⁴⁹ However, as shown in Figure S1, Supporting Information (SI), applying a U-correction to oxygen makes the energy level alignment with the vacuum significantly worse, and work function predictions end up with overestimating the experimental/hybrid functional values by more than 1 eV. W 4f core level binding energy values were determined within the final state approximation, using the ultrasoft pseudopotentials available from the PSLibrary version 0.3.1,⁵⁰ and building a W pseudopotential with a hole in the 4f core orbital using the LD1 atomic code of Quantum Espresso. The plane-wave and charge density cutoffs used for these pseudopotentials were 50/250 Rydberg, respectively. Due to the strain imposed by the 4x4 supercell used, the phonon frequencies were found to be up to 5meV wrong for the modes parallel to the surface, by comparing the free standing WO₃ bilayers in their optimal/expanded lattice parameters. To get more quantitatively accurate values, a bigger 18.53x18.53Å supercell was employed, with a 5x5 WO₃ bilayer rotated w.r.t. the Ag(100) surface by 6.34°. In this supercell, the strain on the WO₃ layer is approximately +0.5%, which gives error in the phonon frequencies of less than 1meV. Ab-initio Molecular Dynamics (AIMD) were then performed within the Born-Oppenheimer approximation with a time step of 1fs at 300K for a total of 12ps. A canonical ensemble with the temperature controlled through velocity rescaling was used in the initial 7ps of the run, then switching to a microcanonical ensemble for additional 5ps, where all averages were performed. The phonon population at 300 K was extracted by doing the Fourier transform of the velocity autocorrelation of the dynamics within the Travis code.⁵¹

3. RESULTS AND DISCUSSION

3.1. Morphology and Structure

Figure 2 shows large-scale STM images illustrating the growth morphology of the W-oxide layer on Ag(100) for various oxide coverages. The WO_3 coverage has been referred to the density of the cubic – $\text{WO}_3(001)$ surface plane, i.e. one monolayer (ML) corresponds to $7.19 \times 10^{14} \text{ cm}^{-2}$. Following the deposition of sub-monolayer WO_3 coverage onto the Ag(100) surface kept at 773 K small 2D oxide islands form which coexist with bare Ag(100) areas (Figure 2a). Most of the WO_3 islands display square contrast patterns with a large corrugation (identified below as Moiré patterns and described in more detail in Figure 3), whereas other oxide islands appear flat in the STM images. This picture persists for increasing the nominal WO_3 coverage above one monolayer (Figure 2b): here only the oxide islands' lateral size have increased, but a closed overlayer on the Ag(100) surface is not formed yet. This is a first indication that the structure of the WO_3 layer on Ag(100) differs from the WO_3 monolayer on Pd(100)³⁸ (see e.g. the structure model in Figure 1c) and consists of more than one atomic WO_3 layer. Indeed, the STM line profile across the 2D WO_3 islands (see inset in Figure 2b) yields an apparent height of $\sim 0.5 \text{ nm}$ (the latter value varies $\pm 0.1 \text{ nm}$ within the bias voltage range of -2.0 to +2.0 V), which is significantly higher than the 0.15 nm height of the WO_3 monolayer on Pd(100).³⁸ The WO_3 layer apparent height on Ag(100) is also in good agreement with the thickness of 0.6 nm estimated from XPS measurements (Figure S2, SI). Another interesting morphological observation from Figures 2a, b is that with increasing the coverage the oxide islands grow laterally not only over the flat Ag terraces, but also across the Ag steps, i.e. the WO_3 growth on Ag(100) follows a carpet-flow mode. The latter is typical for weak film-substrate interactions, and this important result will be supported by other structural properties of the WO_3 layer and discussed in more detail below.

Figure 2. STM images of the 2D WO₃ layer on Ag(100): (a) 0.7 ML (150 × 150 nm², +0.5 V, 0.1 nA); (b) 1.4 ML (150 × 150 nm², +0.8 V, 0.2 nA). A line profile measured along the yellow line in (b) is shown in the inset. The WO₃ islands and the bare Ag areas are indicated; (c) Large-scale STM image of a 2.0 ML wetting WO₃ layer on Ag(100) (300 × 300 nm², +1.4 V, 0.1 nA); (d) Zoom-in image (30 × 30 nm², +0.5 V, 0.4 nA) of the WO₃ surface in (c). The images (a), (b) and (c) have been differentially filtered to enhance the topographic contrast.

The large-scale (300 nm x 300 nm) STM image in Figure 2c has been taken after the deposition of nominally 2 monolayers (ML) WO₃ on the Ag(100) surface and reveals a well-ordered and atomically flat wetting layer. Figure 2d presents a zoom-in STM image, where both the square WO₃ atomic structure (lattice parameter $a = 3.7 \pm 0.1 \text{ \AA}$) and the Moiré pattern (with a periodicity $A = 37.0 \pm 0.2 \text{ \AA}$) are clearly resolved. The Moiré pattern results from the superposition of the Ag(100) substrate (lattice parameter of 2.89 Å) and the square oxide film lattice. Despite the large lattice mismatch of $\sim 7.6\%$ to the Ag(100) surface the WO₃ layer is nearly defect-free and extends over a large surface area, which is an additional evidence in favor of the weak film-support coupling. Few small oxide islands with an apparent height of $\sim 1 \text{ nm}$ can be seen on top of the WO₃ layer and indicate the beginning of next oxide layers' growth.⁵² This growth behavior is supported by the XPS results shown in Figure S2 (SI). In particular, the W 4f peak area increases linearly with the oxide coverage up to 2 ML, at which the 2D WO₃ layer completely covers the Ag(100) substrate. Above this coverage there is a break in the slope of the uptake curve, which marks the transition between 2D and bulk-like oxide film growth.

We can thus conclude that a 2D WO₃ bilayer can be prepared on Ag(100), which exhibits large-scale planar dimensions and is weakly coupled to metal substrate.

To obtain an exact value of the lattice parameter of the 2D WO₃ layer, the Moiré – structure has been analyzed in detail. Figure 3a shows a large scale STM image of 1.5 ML WO₃ on Ag(100), where several islands displaying a great variety of Moiré patterns are present. The corresponding LEED pattern (Figure 3b) exhibits a coexistence of numerous diffraction spots arranged along a circle, originating from different rotational orientations of the 2D WO₃ lattice vectors with respect to the underlying Ag(100) lattice. The WO₃ bilayer thus grows rotationally-disordered on the Ag(100) surface, which is fully in line with the previous findings. There are only few preferred orientations, such as 45°, 35°, 26° and 0°, which yield sharp LEED reflections and correspond to the largest oxide islands in Figure 3a, indicated a, b, c and d, respectively.

Figure 3. (a) Large-scale STM image ($300 \times 300 \text{ nm}^2$, +1.2 V, 0.1 nA) of 1.5 ML WO₃ layer on Ag(100) displaying different rotational islands, indicated a - d; (b) corresponding LEED pattern ($E = 50 \text{ eV}$), the arrows indicate the Ag(100) reciprocal unit cell.

High-resolution STM images of the latter islands are presented in Figures 4(a – d), where both the atomic – and Moiré – lattices are well resolved. The 45° - rotated WO₃ islands constitute the major part and are characterized with a square Moiré pattern with the largest periodicity of 38 Å and corrugation amplitude of 0.4 Å (Figure 4a). In contrast, no Moiré pattern can be

observed for the 26° - rotated WO_3 islands, the corresponding STM images (Figure 4c) display only an atomic lattice contrast.

Figure 4. (a) Large-scale STM image ($300 \times 300 \text{ nm}^2$, +1.2 V, 0.1 nA) of 1.5 ML WO_3 layer on Ag(100) displaying different rotational islands, indicated c - f; (b) corresponding LEED pattern ($E = 50 \text{ eV}$), the arrows indicate the Ag(100) reciprocal unit cell; (c-f) Atomically-resolved STM images of the corresponding islands in (a) with rotational angles of 45° (c), 35° (d), 26° (e), and 0° (f). The calculated Moiré patterns for the different orientations are superimposed onto the STM images.

Accurate measurement of the lattice constant of surface structures by STM is generally difficult due to piezo non-linearity and thermal drift distortions. Fortunately, in the presence of well-resolved atomic – and Moiré – lattices in the images, both will be influenced to the same degree by the distortions, which allows their self-consistent correction and eventually obtaining an accurate structural information. The determination of the lattice parameter of the 2D WO_3 layer is performed using a fitting procedure of the experimentally measured Moiré patterns by simulated amplitude maps.⁵³ The latter are displayed in the insets of Figures 3a, b and d for the corresponding rotational angles and they reproduce very well both the experimental contrast

and periodicity. Applying the optimization procedure to the different Moiré patterns, where the WO_3 lattice constant and the rotation angle between overlayer and substrate lattices are adjustable parameters, yields a value of $3.72 \pm 0.05 \text{ \AA}$.⁵³ A similar number ($3.73 \text{ \AA}$) has been obtained from analyzing LEED intensity profiles taken in directions along the Ag(100) reciprocal unit cell vectors (Figure 3b), i.e. including the Ag reflections for length scale referencing. The lattice parameter of the WO_3 bilayer is close, but importantly, somewhat smaller than the bulk cubic- WO_3 value ($a = 3.77 \text{ \AA}$). Note that free – standing ultrathin oxide layers are theoretically predicted to be contracted,⁵⁴ due to the enhanced intra-layer bonding, and this is a further evidence for the weak WO_3 overlayer – Ag substrate interactions.

3.2. Spectroscopic Characterization

High-resolution XPS W 4f and O 1s core-level spectra (Figure S3, SI) suggest that the 2D W-oxide layer on Ag(100) exhibits a WO_3 stoichiometry. This conclusion is supported by the fact that no oxygen loss has been detected in the O 1s spectra (Figure S3b) during the transformation of intact $(\text{WO}_3)_3$ clusters into a compact 2D WO_3 layer upon UHV annealing to 773 K. Figure 5a shows W 4f core level spectra of the WO_3 bilayer on Ag(100) taken at normal emission and at two photon energies of 140 eV and 450 eV, which are exciting photoelectrons with kinetic energies of $\sim 105 \text{ eV}$ and 415 eV , originating from different WO_3 probing depths of 4.8 and 9.4 $\text{\AA}$, respectively.⁵⁵ W 4f spectra of bulk WO_3 compounds are typically characterized by a spin-orbit $4f_{7/2} - 4f_{5/2}$ doublet with binding energies of 36.0 eV and 38.15 eV and a peak ratio of 4:3, respectively.⁵⁶ The W 4f spectra of the 2D WO_3 layer on Ag show a more complex line shape, which has been decomposed into three different doublet components with W $4f_{7/2}$ binding energies of 36.1 eV, 35.0 eV and 34.2 eV, indicated **A**, **B**, and **C**, and displaying full widths at half maximum (FWHM) of 1.4 eV, 1.3 eV and 0.6 eV, respectively. Formally, the W $4f_{7/2}$

binding energies of the **B** - and **C** - components would indicate the presence of W species with reduced oxidation states of 5+ and 4+ in bulk W-oxides⁵⁶ (which would contradict the WO₃ layer stoichiometry), but in ultrathin oxide films such assignment is not adequate due to the proximity of the underlying metal substrate and corresponding differential initial and final state effects.⁵⁷

Figure 5. (a) W 4f core level spectra of the WO₃ bilayer on Ag(100) taken at two photon energies of 140 eV and 450 eV. The W 4f are decomposed into three different doublet components, indicated A, B, and C, described in the text. The circles correspond to the experimental data, the solid curves to the fit; (b) Charge density difference between the combined WO₃/Ag(100) system and its isolated metal and oxide counterparts. Loss/gain of electrons is represented in blue/red, respectively. The numbers in (b) denote the Bader charge differences with respect to a relaxed isolated WO₃ bilayer/Ag surface.

The photon energy dependence of the intensities of the different W 4f core level components in Figure 5a helps in identifying their physical origin. In the W 4f spectrum taken at a photon energy of 450 eV, i.e. at less surface sensitive detection conditions, the **B** - component gains in intensity at the expense of the **A** – and **C** -components. This is a clear indication that **B** is due to deeper lying W atoms, i.e. located near the oxide – metal interface, whereas **A** and **C** originate from W atoms near or at the oxide surface.

The Bader charge density analysis in Figure 5b (discussed in more detail below) shows that the lower binding energy of the **B** - component with respect to the **A** - component can be related to the stronger electron transfer from the Ag substrate to the interfacial than to the surface W and O atoms and is a result of both initial and final state effects. The physical nature of the **C** - component is less clear at present. It is unlikely to associate this sharp peak with a conspicuously low binding energy of 34.2 eV with some defects at the surface of the otherwise fully stoichiometric and structurally well-ordered WO₃ layer. Interestingly, W 4f spectra of tungsten bronzes, Na_xWO₃, exhibit a very similar fine structure, whose interpretation was a matter of long debate.⁵⁸⁻⁶² The most conceivable analysis is due to Wertheim, who proposed that the complex W 4f spectral shape in Na_xWO₃ can be described by two different final state spin-orbit doublets, which are “screened” and “unscreened” by the itinerant Na conduction band electrons.^{61,62} The screened fundamental line is at low binding energies and particularly narrow, whereas the unscreened satellite is shifted by ~ 2eV to higher binding energies and exhibits a significant lifetime-broadened peak shape. We believe that similar arguments may also apply for the WO₃ bilayer on Ag(100), where the role of the screening media of the W 4f core hole is played by the conduction electrons in the Ag substrate. The surface **A** - and **C** - components would thus be attributed to poor and well screened W 4f final states, respectively, whose peak shapes and energy separation (1.9 eV) are indeed very similar to those in tungsten bronzes.

The work function of the WO₃ layers on Ag(100) increases with the WO₃ coverage from the value of 4.55 eV of the clean Ag(100) surface to 6.20 eV upon completing the WO₃ bilayer. The latter value is in good agreement with the theoretically predicted one, as discussed below.

HREELS spectra of the 2D WO₃ bilayer on Ag(100) are reported in Figure 6 in the range of phonon (a) and electron (b) excitations. In Fig. 6a the phonon spectrum of the WO₃ monolayer on Pd(100), adopted from Ref. 38, is shown for comparison. Both phonon loss spectra contain

a sharp and intense peak at a frequency of ~ 125 meV, which is characteristic for the stretching vibrations of terminal W=O species.³⁸ The vibrational bands at 95 meV and 52 meV in the HREELS spectrum of the WO₃ monolayer on Pd, which have been assigned to the in-plane and out-of-plane basal O atoms, respectively (see monolayer WO₃ structure model in Fig. 1c),³⁸ are also present in the spectrum of the WO₃ bilayer on Ag. This is not surprising since these vibrations originate from O atoms in the surface oxide layer, whose structure is identical in the WO₃ films on both substrates (see structure model of the WO₃ bilayer on Ag(100) in Fig. 7). There are however some important differences: in the phonon loss spectrum of the WO₃ bilayer the W=O stretching vibration exhibits a significant broadening towards lower loss energies, and there is an additional vibrational band centered around 70 meV. These new features are associated with vibrational modes of O atoms in the internal oxygen layers of the WO₃ bilayer, as it will be shown in the detailed layer-resolved analysis of the vibrational spectrum below (see e.g. Figure 9).

Figure 6. HREELS spectra of the WO₃ bilayer on Ag(100) (in black) taken in the phonon (a) and electron (b) excitation regions. The primary electron energy and energy resolution are 4 eV and 4.4 meV in (a) and 26 eV and 25 meV in (b). The phonon loss spectrum of the WO₃ monolayer on Pd(100) (adopted from Ref. 38) is shown as a blue line in Figure 6a for comparison. A magnified part of the electron loss spectrum in Figure 6b is shown in the inset.

An electron energy loss spectrum of the 2D WO₃ layer on Ag(100) is depicted in Figure 6b. Close to the elastic peak a broad tail is visible, which extends to ~ 2.5 eV and is characteristic of electron transitions between the Fermi level and a continuum of unoccupied states, indicating the absence of a band gap in the WO₃/Ag system, in good agreement with the calculated projected density of states (PDOS) shown in Figure 8. At 3.45 eV a sharp loss peak is observed, which can be associated with an inter-band transition between the filled O 2p and empty W 5d states (see Figure 8c).

3.3. Structure model and theoretical analysis

DFT in the supercell approximation has been used to investigate the energetics and single out the most stable structures of monolayer and bilayer WO₃/Ag(100) systems, illustrated in Figure S4, SI. Our first conclusion from this study is that WO₃ prefers to grow on Ag(100) as a bilayer, rather than a monolayer. This is basically due to the relative weakness of the WO₃/Ag interaction and the larger lattice parameters of the bilayer entailing a smaller lattice mismatch with the metallic substrate. In fact, the optimized lateral lattice parameter of the free-standing monolayer, bilayer, and bulk WO₃ structures were determined as 3.71, 3.76, and 3.81 Å, respectively. This rationalizes the experimental observation of a WO₃ bilayer with a lateral lattice slightly compressed with respect to the bulk. Our second major finding is that the energetically favored structure of the bilayer does not correspond to a piece of monoclinic bulk WO₃, but has the bottom layer exhibiting inverted WO₆ octahedra and shifted by half a unit lattice with respect to the top one, see Figures 7a and 7b for a direct comparison between these two models. This structure turns out to be favored in the unsupported case by 182 meV per WO₃ unit, and still remains more stable when grown on Ag(100) by 93 meV. Our proposed structural model is favored because it exhibits perfectly symmetric WO₆ octahedra for all W

atoms in both layers, while the bulk extracted structure leads to the formation of both WO_6 octahedra and WO_5 truncated octahedra, leaving half of the W atoms with a dangling oxygen bond. This is also reflected in the electronic structure of each configuration in the unsupported case, where we get shell closure and a large 0.9 eV energy gap for the most stable case, compared to a nearly zero gap found for the bilayers extracted from the monoclinic WO_3 bulk. We note that the band gap value of 0.9 eV is likely underestimated, which is in keeping with the known tendency of the PBE xc-functional to underestimate band gaps. The nonpolar character of the inverted bottom layer configuration also plays a role in stabilizing it. We finally note that this bilayer model in the free-standing case is very stable, when different conditions of oxygen pressure and temperature are considered, as illustrated in Figure S5, SI.

Figure 7. Side views of the unsupported WO_3 bilayer extracted from the WO_3 monoclinic (a) and $\alpha\text{-MoO}_3(010)$ (b) bulk structures; (c) A side view of the $\alpha\text{-MoO}_3(010)$ structure model. The MoO_3 bilayer is highlighted; Top (d) and side (e) views of the DFT structure model of the WO_3 bilayer on $\text{Ag}(100)$. The WO_3 surface unit cell is colored with a yellow square in (d). W, O, Mo and Ag atoms are shown in blue, red, dark-gray, and light-gray, respectively.

Interestingly, our proposed structural model is akin to a slab of the bulk α - MoO_3 , illustrated in Figure 7c. The fact that α - MoO_3 is a layered compound and the distinct energetic stability of the proposed model leads us to hypothesize that the WO_3 bilayer structure should be a general model for WO_3 systems confined at the 2D limit (nanosheets, etc.). Top and side views of the proposed WO_3 bilayer model supported on Ag(001) are shown in Figures 7d and 7e, respectively, and its electronic and structural properties are discussed next.

The predicted properties of our structural model are overall in very good agreement with experiment, with the exception of core level energies, where the agreement is fair due to complex many-body final state effects. The optimized layer thickness is 6.44 Å, very similar to the experimental XPS estimation of ~ 6 Å. At the interface, the average Ag-O distance and its mean deviation are (2.4 ± 0.2) Å, significantly lower than in the monolayer case, equal to (2.6 ± 0.2) Å, which further confirms that the formation of a second layer stabilizes the system, increasing its very weak interaction with the substrate. Indeed, the formation energy H , defined as:

$$H = E_T - E[\text{Ag}] - N E[(\text{WO}_3)_3],$$

where E_T is the total energy, $E[\text{Ag}]$ the energy of the non-interacting Ag(100), $E[(\text{WO}_3)_3]$ the energy of a $(\text{WO}_3)_3$ unit adsorbed on Ag and N the number of WO_3 units, was found to be -880 meV/ WO_3 unit for the monolayer, and -927 meV/ WO_3 unit for the bilayer. A Bader charge analysis, shown in Figure 5b, reveals that there is a charge donation from the Ag support to the WO_3 bilayer film, with the donated charge essentially localized at the interface oxygen and 1st layer tungsten atoms, therefore explaining the lower binding energy of their core level peaks. A comparison of the Projected Density of States (PDOS) of the system with that of the fragment Ag(001) and free standing WO_3 bilayer (see Figure 8) shows that deposition changes significantly the electronic structure of the WO_3 film. The gap found for the free-standing bilayer disappears, with the Fermi region showing contributions of mostly W and Ag states.

Furthermore, the O highest occupied states show an overall 0.2 eV positive shift with respect to the vacuum, while the unoccupied W states closest to the Fermi energy show a 0.3 eV negative shift, shortening their distance with respect to the free-standing case. We have also analyzed the PDOS of the W atoms of the supported and free-standing bilayer films with respect to the vacuum level, shown in Figure S6, SI. From this figure we extract an overall +0.2 eV shift of W states for supported bilayer, which, given the small 0.14 eV electron charge transfer from Ag to the oxide, falls in the same order of magnitude predicted in a recent work by J. Goniakowski et. al.⁶³, and this further confirms the weak nature of the metal-oxide interaction.

Figure 8. Projected density of states for (a) the isolated Ag(100) surface (b) the free WO₃ bilayer (Figure 7b), and (c) the supported WO₃/Ag system (Figures 7d,e). The contribution of W, O, and Ag atoms, are shown in blue, red and black, respectively. Filled/empty curves represent occupied/empty states. The zero energy was set as the highest occupied molecular orbital (HOMO). The relative HOMO value (in eV) with respect to 0 eV vacuum level is, for (a), (b), and (c), equal to 4.3, 8.3, and 6.6eV, respectively.

Simulated STM images of the WO₃ bilayer are shown in Figure S7, SI, and they reveal that the outermost oxygen atoms are imaged bright in STM. The simulated images at 0° and 45° reproduce well the corresponding moiré patterns observed experimentally (Figure 4).

The predicted work function (WF) of WO₃/Ag(100) is 6.6 eV, in between the predicted WF for clean Ag(100) (4.3eV) and the free standing WO₃ bilayer (7.43eV < WF < 8.3eV), and is only

slightly overestimated with respect to the experimental value (6.2 eV). The W 4f core level energies were also simulated, and the difference between the core level energies of the W atoms at the interface and in the top surface layer resulted to be (0.31 ± 0.02) eV, in qualitative agreement with the experimental results of Figure 5a (we are presently unable to simulate the complex excitation phenomenon likely giving rise to peak C). We note here that both the overestimation of the work function and the underestimation of the W 4f core level experimental values could be connected to the fact that we consider only one orientation of our structure with respect to the substrate, whereas experimental values are, in fact, an average over many different orientations. Limitations of our DFT+U approach could also be a source of theory/experiment discrepancy (the use of more accurate and also expensive xc-functionals is beyond our present computational capabilities).

We finally performed Ab Initio Molecular Dynamics (AIMD) and evaluated atomic velocity auto-correlation to extract phonons at 300 K, see Figure 9. Here we distinguish the contribution of the perpendicular “z” modes of the outermost oxygen atoms (in purple and blue) from the contribution of the parallel “xy” modes of the internal oxygen atoms (in yellow and pink): the perpendicular modes should have an enhanced intensity due to interaction with image charges in the metallic substrate. Five different spectroscopic regions are predicted: Region 1: a narrow peak centered at 128 meV corresponding to the perpendicular W-O vibrations of the external oxygen atoms; Region 2: three peaks at 107/114/117 meV corresponding to perpendicular W-O vibrations of the interface oxygen atoms, with the difference in the frequencies connected to the position of the interface-O atoms w.r.t. the Ag support, i.e., on top (107 meV), bridge (114 meV) or hollow (117 meV) positions; Region 3: two peaks centered at 99/104 meV corresponding to parallel W-O vibrations of the internal oxygen atoms and comprising coupled modes with contributions from both internal layers (yellow and pink); Region 4: two large peaks at 80/85 meV, corresponding to parallel W-O vibrations of the internal oxygen atoms,

uncoupled and slightly different for the internal layer (yellow) w.r.t. the 2nd layer (pink); Region 5: a single peak centered at 70 meV corresponding to parallel W-O modes involving coupled modes of both internal oxygen layers.

Figure 9. (a) Side view of the supercell used in the AIMD run, coloring the first/second/third/fourth oxygen layers is in red/yellow/pink/blue, respectively. (b) Phonon population as a function of the frequency, same color scheme. The total spectrum is in black, and five different sectors are highlighted, described in the text.

These results are in excellent agreement with the experimental HREELS measurements for the Ag/Pd-supported system in Figure 6a. In region 1, the small increase in the W=O stretching frequency from Pd to Ag is reproduced well in our calculations (128 meV for Ag versus 124 meV for Pd³⁸). Region 2 shows a broad peak at (115±5) meV for WO₃/Ag, absent in WO₃/Pd, which is similar to the theoretically simulated peak, and is interpreted as perpendicular W=O stretching modes at the interface, not present in the WO₃ monolayer on Pd. The experimental peak around 70 meV for WO₃/Ag is theoretically explained with coupled parallel internal modes of the WO₃ bilayer (region 5), which do not exist in the WO₃/Pd system, due to its monolayer coverage.

4. CONCLUSIONS

A 2D $\text{WO}_3(001)$ – type phase has been prepared on a $\text{Ag}(100)$ surface by an MBE technique in UHV and has been characterized experimentally at the atomic level by state-of-the-art surface science techniques (STM, LEED, XPS, UPS, HREELS), as well as theoretically by a DFT + U approach. The 2D WO_3 forms an incommensurate crystalline overlayer that grows in various rotational orientations: this is indicative of a weak oxide – substrate coupling. The experimentally determined 2D square lattice parameter is $a_{2D} = 3.72 \text{ \AA}$, which is close to the $a_{3D} = 3.78 \text{ \AA}$ value of cubic WO_3 . However, the most stable 2D structure determined by DFT consists of a WO_3 bilayer formed by a staggered arrangement of WO_6 octahedra, linked together by corner and edge sharing. This structure is non-native and unrelated to the cubic or monoclinic WO_3 bulk lattices, but is akin to a bilayer of the $\alpha\text{-MoO}_3$ structure. The experimental results are in full agreement with the DFT derived bilayer structure model. A thorough analysis of the phonon structure has been performed, with excellent experiment – theory agreement, in support of the proposed model. The 2D WO_3 bilayer of the $\alpha\text{-MoO}_3$ – structure – type on $\text{Ag}(100)$ is a robust structure, which according to the DFT calculations should also survive as a stable structure without a support. We therefore propose that the WO_3 bilayer structure is also a serious candidate for the structure of free – standing WO_3 nanosheets, prepared by wet-chemical synthesis methods and with emerging applications in a variety of advanced nanotechnology fields.⁶⁴

ASSOCIATED CONTENT

Supporting Information

Density of states (Figures S1 and S6), XPS spectra (Figures S2 and S3), DFT structure models (Figure S4 and Table 1), energy stability diagram (Figure S5), simulated STM images (Figure S7) and phonon density of states (Figure S8).

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Notes

The authors declare no competing financial interest.

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