Interaction of Na with 2D WO₃ and MoO₃ Layers on Pd(100): From Doping to 2D Bronze Formation

Malike Mohammadi, Fabio R. Negreiros,* Thomas Radlinger, Philip Edelmayer, Falko P. Netzer, and Svetlozar Surnev*

Cite This: J. Phys. Chem. C 2022, 126, 3289−3300

ABSTRACT: Doping of tungsten trioxide (WO₃) and molybdenum trioxide (MoO₃) materials with alkali atoms, leading to the formation of the so-called sodium bronzes, is a viable approach to achieve a precise control of their electronic, optical, and magnetic properties via electron band structure engineering. Driven by the ongoing trend for thickness reduction and the resulting new functionalities at the nanoscale, using a combination of state-of-the-art experimental and computational techniques, we investigate here the interaction of two isostructural two-dimensional (2D) WO₃ and MoO₃ layers, grown epitaxially onto a Pd(100) surface, with Na dopants. We identify two interaction regimes as a function of the Na coverage: a low-coverage regime up to 0.3 ML, which we describe in terms of doping interactions, and a reaction regime, where at higher Na coverages, the 2D WO₃/MoO₃ lattices become destroyed and several ordered 2D bronze-type phases form upon thermal activation. In the doping regime, Na initially decorates the oxide domain boundaries and later adsorbs in a (2 × 2) superstructure, filling the regular adsorption sites within the oxide domains. Further Na accommodation in the 2D oxide lattice is unfavorable due to the poor lateral electrostatic screening and elastic strain increase. In the reaction regime, the most prominent and energetically stable phase is the hexagonal 2D bronze-like layer, whose atomic details are resolved in a density functional theory (DFT) analysis and compared with the structure of the bulk counterpart.

1. INTRODUCTION

WO₃ and MoO₃ are oxide materials of special interest, featuring a variety of structural phenomena and polymorphs and versatile functionalities with many attractive properties for applications in diverse technologies. The structure of WO₃ may be derived from the cubic ReO₃ lattice, with WO₆ octahedra corner-sharing and located at the corners of a cube. However, as a result of symmetry reduction due to the distortion and tilting of the octahedra, a plethora of lower-symmetry structures has been detected as a function of temperature. At room temperature, a monoclinic structure is the most stable. For MoO₃, the layered α-phase is thermodynamically stable, consisting of edge and corner-sharing MoO₆ octahedra linked to create layered sheets that are stacked in the [010] direction. In addition to the orthorhombic α-phase, a metastable monoclinic β-phase, similar to the room-temperature WO₃ phase, has been reported. WO₃ and MoO₃ find applications in the fields of catalysis, photocatalysis, electronic devices in energy-related green technology applications, such as electrochromic and smart window technology, and sensing platforms to name just a few. Recently, the preparation of WO₃ and MoO₃ nanosheets, that is, two-dimensional (2D) free-standing materials consisting of ultrathin one-to-several atomic layer thick structures, has attracted considerable interest. As a result of their high surface-to-volume ratio and thickness confinement, novel features are encountered and attractive applications for these 2D materials in nanotechnology have been envisioned. The reported preparation procedures of the 2D nanosheets, mostly of a wet-chemical nature, have the advantage of being simple and cheap and the disadvantage of lacking reproducible control over atomic thickness, shape, and uniformity of the sheet structures. In the present work, we report the fabrication of 2D WO₃ and MoO₃ materials supported on a metal surface by molecular-beam epitaxy (MBE) growth, which allows a precise atomic control over the structure and morphology. The structure and electronic properties of oxides are highly tunable by doping with foreign atoms, leading to band gap engineering of semiconducting oxides, such as WO₃ and MoO₃, by shifting the valence and conduction band edges and introducing new electronic states. Of particular relevance is the doping of WO₃ and MoO₃ with alkali atoms, which leads to the formation of the alkali bronzes via intercalation of the alkali species into the cavities of the oxide lattice. The alkali-tungsten bronzes occur mainly in two polymorphs, (near-)cubic and hexagonal. In the “cubic perovskite structure approximation”, the alkali metal atoms occupy the vacant A...
sites of the ABO₃ lattice, whereas in the hexagonal structure, the alkali atoms are located in the hexagonal channels formed by the W(Mo)O₆ octahedra. The Na₂WO₃ are the most stable and also most studied cubic tungsten bronzes, whereas the larger alkali cations become more stable in the hexagonal polymorphs. The alkali bronzes display some extraordinary optoelectronic properties due to the electron transfer from the alkali atoms to oxide host states. For Na₂WO₃, the visual appearance goes from green through gray, blue, purple, red, and orange to yellow as x increases from 0 to 1. The Na₂WO₃ supports an insulator-to-metal transition at x ∼ 0.25, whose origin has been debated, but the discussion appears to converge in favor of an Anderson localization model as a result of the statistical occupation of the A sites with Na cations at low x. Besides electronic effects, the incorporation of alkali ions into WO₃ also has structural effects, with a gradual increase of the lattice constant and structural transformations toward higher symmetry phases, eventually cubic, with increasing doping levels.

Depending on the identity and concentration of the A cations, the blue, red, and purple Mo bronzes have been obtained. In contrast to the W bronzes, which have relatively simple three-dimensional (3D) structures, the Mo bronzes tend to have more complex structures, among them layered-type structures with edge- and corner-sharing MoO₆ octahedra forming infinite 2D sheets held together by A cations, featuring low-dimensional behavior (e.g., charge density wave phases). But alkali Mo bronzes that are isostructural with W bronzes have also been prepared.28,30,31

Here, we present two model systems, consisting of well-ordered 2D WO₃ (MoO₃) layers grown epitaxially on a Pd(100) surface, to study the interaction with Na dopant atoms in the oxide 2D limit. The interaction of 2D oxides with dopant atoms is of interest in view of the ongoing trend for thickness reduction of the active layers in green energy nanodevices. We have used state-of-the-art experimental surface science techniques, such as low energy electron diffraction (LEED), scanning tunneling microscopy (STM), X-ray and UV photoelectron spectroscopy (XPS, UPS), and work function measurements, as well as DFT calculations, to investigate the influence of the Na dopant atoms on the oxide structure, on the chemistry of the surface, and we address the dopant location and the charge transfer dopant-oxide as a structure, on the chemistry of the surface, and we address the investigate the in work function measurements, as well as DFT calculations, to X-ray and UV photoelectron spectroscopy (XPS, UPS), and level in previous work, as detailed below. The 2D MoO₃ unit cell on Pd(100) was determined from the secondary electron cut-offs in the UPS spectra. The Pd(100) surfaces were cleaned by cycles of Ar-ion sputtering and annealing to 1000 K. The 2D WO₃/MoO₃ monolayers were prepared by the deposition of (WO₃)₃/(MoO₃)₃ clusters in UHV onto the clean Pd(100) surface kept at 300 K, followed by annealing at 673 K in 5 × 10⁻⁷ mbar O₂ for 5 min. The (WO₃)₃/(MoO₃)₃ cluster beams were generated by thermal sublimation of WO₃/MoO₃ powders at ∼1250/750 K in Knudsen cell type evaporators. The vaporization flux was monitored by a quartz-crystal microbalance (QMB), measuring the change in the mass of the crystal via the change of the resonance frequency; a change of the frequency by 1 Hz corresponds to a mass change of 10⁻⁸ g cm⁻². The evaporated amount of (WO₃)₃/(MoO₃)₃ is given in monolayers (MLs), whereby one ML is defined by the density of the c(2 × 2)-WO₃/MoO₃ surface planes with a lattice constant of 3.89 Å (i.e., 6.61 × 10⁻¹⁴ WO₃/MoO₃ units cm⁻²). Taking the molecular masses of the WO₃/MoO₃ into account, 1 ML WO₃/MoO₃ on Pd(100) corresponds to a frequency change in the QMB of 25.5/15.8 Hz, respectively. Sodium (Na) was deposited from a commercial SAES getter integrated into a home-built evaporator. Due to the high chemical reactivity of Na, reliable measurement of the Na coverage by QMB is not possible. Here, we took advantage of the universal behavior of the work function with the alkali coverage on metals and calibrated the Na coverage by comparing the experimental work function–Na deposition time and calculated work function–Na coverage curves on Pd(100), as described in more detail in SI (Figure S1b). We define 1 ML Na coverage as one Na atom per one 2D WO₃/MoO₃ unit cell on Pd(100).

2. METHODS

2.1. Experimental Section. The STM experiments were performed in a custom-designed UHV system, equipped with a variable-temperature STM (Oxford Instruments), LEED optics, evaporators for WO₃/MoO₃ and Na deposition, quartz microbalance, and the typical facilities for sample manipulation and cleaning. In the present measurements, STM was operated at room temperature in a constant current mode using electrochemically etched tungsten tips. Positive bias voltages correspond to tunneling into the empty states of the sample. The work function change, ΔΦ, was measured by determining the shift of retarding potential V–V curves using the LEED optics, as shown in more detail in Figure S1a, Supporting Information (SI). For this purpose, the LEED electronics was modified according to the method proposed by Fritz and Haque. The accuracy in determining the work function change amounts to ±0.05 eV.

XPS and UPS measurements were conducted in a second UHV chamber equipped with a dual X-ray source for Mg Kα and Al Kα radiation, a He discharge lamp for He I and He II radiation, and a hemispherical electron analyzer (PHOIBOS 100, SPECS). Typically, Mg Kα radiation was used to excite the W 4f Mo 3d and Na 1s core levels, whereas Na KLL Auger electron spectra were excited by Al Kα to avoid overlap with other XPS or Auger peaks. The absolute work function values were determined from the secondary electron cut-offs in the UPS spectra.

The Pd(100) surfaces were cleaned by cycles of Ar-ion sputtering and annealing to 1000 K. The 2D WO₃/MoO₃ monolayers were prepared by the deposition of (WO₃)₃/(MoO₃)₃ clusters in UHV onto the clean Pd(100) surface kept at 300 K, followed by annealing at 673 K in 5 × 10⁻⁷ mbar O₂ for 5 min. The (WO₃)₃/(MoO₃)₃ cluster beams were generated by thermal sublimation of WO₃/MoO₃ powders at ∼1250/750 K in Knudsen cell type evaporators. The vaporization flux was monitored by a quartz-crystal microbalance (QMB), measuring the change in the mass of the crystal via the change of the resonance frequency; a change of the frequency by 1 Hz corresponds to a mass change of 10⁻⁸ g cm⁻². The evaporated amount of (WO₃)₃/(MoO₃)₃ is given in monolayers (MLs), whereby one ML is defined by the density of the c(2 × 2)-WO₃/MoO₃ surface planes with a lattice constant of 3.89 Å (i.e., 6.61 × 10⁻¹⁴ WO₃/MoO₃ units cm⁻²). Taking the molecular masses of the WO₃/MoO₃ into account, 1 ML WO₃/MoO₃ on Pd(100) corresponds to a frequency change in the QMB of 25.5/15.8 Hz, respectively. Sodium (Na) was deposited from a commercial SAES getter integrated into a home-built evaporator. Due to the high chemical reactivity of Na, reliable measurement of the Na coverage by QMB is not possible. Here, we took advantage of the universal behavior of the work function with the alkali coverage on metals and calibrated the Na coverage by comparing the experimental work function–Na deposition time and calculated work function–Na coverage curves on Pd(100), as described in more detail in SI (Figure S1b). We define 1 ML Na coverage as one Na atom per one 2D WO₃/MoO₃ unit cell on Pd(100).

2.2. DFT Calculations. Density functional theory (DFT) calculations were performed using the open-source Quantum Espresso (QE) package and the PBESOL exchange–correlation functional. Several supercells were used to study the different Na coverage regimes, and their details are given in the text as they are introduced. For all supercells, the Pd(100) substrate was simulated with three layers, where the bottom two were kept fixed in their bulk positions. In addition, 22 Å of vacuum-separated periodic images in the perpendicular...
direction and dipole corrections were included. A Gaussian smearing of 0.04 eV was used, and the reciprocal space was sampled with a Monkhorst−Pack mesh, with a grid size of $12 \times 12 \times 1$ at an area of 7.5 Å$^2$, and proportionally smaller as the supercell size increases. A Hubbard correction of 6 eV was used for W, for consistency with previous works, and 4 eV for Mo, evaluated with density functional perturbation theory within QE. A spin-unrestricted formalism was adopted. The work function, projected density of states (PDOS), simulated STM properties, and Lowdin charge analysis were evaluated within QE, while the Bader/Voronoi atomic charges were evaluated with the Henkelman’s code. The Na chemical potential $\mu_{\text{Na}}$ used to evaluate the Na adsorption energies, was calculated as $\mu_{\text{Na}} = \frac{E(\text{Na}_2\text{O}) - E(\text{O}_2)}{2}$, where $E(\text{Na}_2\text{O})$ is the energy of the cubic bulk oxide Na$_2$O, and $E(\text{O}_2)$ is the energy of an isolated oxygen molecule, corrected to give its experimental binding energy. The same reference ($E(\text{O}_2)$) was used to calculate the energy to create oxygen vacancies, and it corresponds to an oxygen-rich limit and, therefore, the values reported represent an upper bound for this value.

3. RESULTS AND DISCUSSION

3.1. 2D Oxide Layers: c(2 $\times$ 2) WO$_3$ and MoO$_3$ Monolayer Phases on Pd(100), WO$_3$ forms a stoichiometric 2D monolayer oxide phase on Pd(100) with a well-ordered c(2 $\times$ 2) structure, as reported previously and illustrated in Figure 1a–c: the high-resolution STM images display bright protrusions delineating the $(\sqrt{2} \times \sqrt{2})$R45° unit cells (Figure 1b,c) and the LEED pattern shows sharp integral order and (1/2, 1/2) order reflections, the latter split into four spots. The

**Figure 1.** LEED patterns of 2D WO$_3$ (a) and MoO$_3$ (d) layers on Pd(100); the electron energy was 50 eV. STM images of the 2D WO$_3$ (b, c) and MoO$_3$ (e, f) layers on Pd(100), illustrating the c(2 $\times$ 2) antiphase domain structure: (b) 30 nm $\times$ 30 nm ($U = +1.4$ V, $I = 50$ pA) and (c) 10 nm $\times$ 10 nm ($U = +1.0$ V, $I = 100$ pA). The c(2 $\times$ 2) unit cell is indicated: (e) 20 nm $\times$ 20 nm ($U = +1.7$ V, $I = 50$ pA) and (f) 10 nm $\times$ 10 nm ($U = +1.1$ V, $I = 100$ pA). A triangular feature at the domain corner is encircled.

**Figure 2.** (a) Supercell was used to simulate a 7 $\times$ 7 WO$_3$/MoO$_3$ square monolayer on Pd(100). The domain size is approximately 3 $\times$ 3 nm$^2$, and the antiphase domains are simulated by rotating the cell vectors with respect to the Pd[100] direction by $\approx 3.8^\circ$. W (Mo) atoms are in blue, while oxygen/palladium are in red/gray, respectively. (b) Top: W−O bond length spatial distribution for the WO$_3$ monolayer only (the Pd substrate is removed for visualization purposes). Bottom: W−O/Mo−O pair distribution function. (c) Projected density of states (PDOS) for WO$_3$/MoO$_3$ on Pd(100) systems. The Fermi energy is set as zero, illustrated with a dashed line.
The $c(2 \times 2)$ structure forms regular square domains separated by dark antiphase domain boundaries, generating a nanoscale domain pattern. The antiphase domain relations are clearly manifested in LEED by the characteristic splitting of the fractional-order reflections. DFT calculations have identified the $c(2 \times 2)$ layer as a $WO_2 + O$ bilayer, as generated by cutting a slice perpendicular to the [100] direction of the cubic $WO_3$ bulk structure (see Figure 2a for a schematic model). The DFT analysis has also rationalized the antiphase domain boundaries as an effective means for the relief of epitaxial strain.

The $MoO_3$ monolayer on Pd(100) shows a strikingly similar behavior to $WO_3$ (Figure 1d–f). The STM images clearly reveal the square $c(2 \times 2)$ domains and the antiphase domain boundaries, which are confirmed by the split 1/2 order reflections of the LEED pattern. Detailed analysis of the $c(2 \times 2)$ LEED pattern of the $WO_3$/Pd(100) surface (Figure 1a) and a number of large-scale STM images has revealed an average domain size of $3.7 \pm 0.5$ nm; the latter has also been substantiated by the DFT modeling of the domain lattice. On a local scale, however, there can be deviations from this average number. The STM images in Figure 1c,f were selected here only for the purpose of demonstrating a good atomic resolution and are not necessarily representative of the average domain size. A similar analysis of the $c(2 \times 2)$ $MoO_3$ LEED pattern (Figure 1d) yields an average domain size of $4.5 \pm 0.5$ nm. This somewhat larger domain size of $MoO_3$ may be understood by considering the epitaxial strain in a similar model for $MoO_3$, as shown in Figure 2. Assuming a symmetric cubic approximation of the metastable monoclinic $\beta$-$MoO_3$ structure (the latter corresponds to a distorted $ReO_3$ lattice), the lattice mismatch for a $c(2 \times 2)$ structure on Pd(100) is less than 1%, as compared to the lattice mismatch for the $WO_3$ $c(2 \times 2)$ lattice of 2.8% (the tensile strain of the overlayers). Less strain results in larger domains, as indeed seen experimentally here for the $c(2 \times 2)$ $MoO_3$ structure.

The W 4f and Mo 3d XPS spectra confirm the similarity of the $WO_3$ and $MoO_3$ $c(2 \times 2)$ phases on Pd(100) (they are presented and discussed in the Supporting Information, Figure S2). The work functions of the monolayer $c(2 \times 2)$ $WO_3$ and $MoO_3$ on Pd(100) surfaces have been measured to be 6.65 and 6.70 eV, respectively.

Previous simulations on $WO_3$ monolayers supported on Pd(100) have provided a detailed structural and electronic description of this system. These calculations, however, did not model details of the antiphase domain boundaries, and in particular the triangular-shaped features observed at the domain corners in the experimental STM images (see Figure 1c,f: one such feature is encircled in Figure 1f). Since corner effects can potentially play an important role in the interaction with Na, we explicitly included them in this work by adopting a more accurate model. The supercell used is detailed in Figure 2a and consists of a square $7 \times 7$ W/Mo oxide monolayer adsorbed on a $7.5 \times 7.5$ Pd(100) surface, where the cell vectors are rotated by $\sim 3.8^\circ$ to simulate the antiphase periodicity. We note that larger domain sizes ($8 \times 8$ for $WO_3$, $10 \times 10$ for $MoO_3$) would give a structure closer to the one found experimentally, but they would also significantly increase the computational costs. We also note that in the pristine model, the domains have an oxygen-termination in all directions and, therefore, present a $XO_3$ stoichiometry with $n$ of approximately 3.3; hence, the X cations at the boundaries are in a very oxidized chemical environment in which oxygen vacancies play an important role.

The spatial distribution of the W–O bond lengths is shown in Figure 2b (top) and reveals 4 types of bonds. The W–O bonds perpendicular to the surface are the shortest ones and are not affected by the domain borders. Those parallel to the surface show three distinct values due to the border effect that shortens/enlarges the parallel W–O bonds of the outermost W/Mo atoms. Therefore, the cations at the boundary are chemically different compared to those inside the domain, as suggested experimentally by the XPS measurements (Figure S2, SI). This qualitative picture is common to both $WO_3$/ $MoO_3$ systems: they present a similar average X–O bond length of approximately 1.915 Å, while the Pd–Pd first neighbor distances are equal up to 0.001 Å. However, the X–O pair distribution function plot (Figure 2b, bottom) reveals that the minimum/maximum X–O bond lengths are smaller/larger for $MoO_3$ than in $WO_3$, suggesting that the strain release is more efficient in the first case. Indeed, the larger domain sizes obtained for $MoO_3$ can be rationalized considering the energy required to laterally expand a free-standing square $XO_3$ monolayer from its optimized lattice to the bulk Pd one, which gives an energy 0.08 eV/ $XO_3$ unit lower for $MoO_3$ compared to $WO_3$ (see Figure S3, SI). The projected density of states (PDOS) in Figure 2c shows an overall similar electronic structure in both systems, with $MoO_3$ being slightly more reducible than $WO_3$, since $WO_3$ has a larger number of empty states right below the Fermi energy, while $MoO_3$ has a larger number of empty states right above it.

The theoretical work function value obtained for $WO_3$ is 6.95 eV, which is 0.3 eV higher than the experimental one. This overestimation is expected, given that the experimental STM images reveal the presence of several oxygen vacancies. Since a single vacancy reduces the work function by 0.05 eV, and the average vacancy population is at least 3 per domain, a good quantitative agreement is actually obtained. This was already pointed out in our previous work. For $MoO_3$, the theoretically predicted work function is 6.70 eV, in excellent agreement with the experimental value.

The triangular features observed at the corners of the $WO_3$ and $MoO_3$ domain boundaries in the STM images in Figure 1c,f can be theoretically understood by noting that the energy to create an oxygen vacancy at the corner is at least 0.45 eV lower compared to creating it in any other domain region, as shown in Figure S4a (SI). This energy can be further reduced by considering a local reconstruction that consists of saturating the dangling X–O bond of the oxygen vacancy using a corner $WO_3$ unit, connecting neighboring domains in the process as illustrated below in Figure 6.

In summary, the DFT calculations confirm the previously proposed $WO_3 + O$ model also for $MoO_3$ on Pd(100). The observation of a cubic $c(2 \times 2)$ 2D $MoO_3$ phase on Pd(100) can be compared to the rectangular $c(4 \times 2)$ $MoO_3$ monolayer phases, which have been reported on Au(111). In the latter case, the symmetry mismatch at the oxide–metal interface leads to a large distortion of the overlayer from the cubic geometry. It is noted in passing that different $\alpha$-$MoO_3$ structure-derived polymorph has been detected for the 2D $WO_3$ phase on Ag(100), where the interlayer coupling is weak.

3.2. Na Dosing. The evolution of the work function is a very sensitive means to follow the deposition of sodium onto the oxide surfaces. Figure 3a shows the change of the work
function $\Delta \Phi$ of the c($2 \times 2$) WO$_3$ and MoO$_3$ on Pd(100) surfaces as a function of the Na coverage ($\Theta_{Na}$). The WO$_3$ and MoO$_3$ layers show similar behavior, although the $\Delta \Phi$ curves differ in quantitative detail. The work functions decrease rapidly upon Na deposition for both WO$_3$ and MoO$_3$, develop a small plateau or change of gradient at around $\Delta \Phi \approx -2$ eV, and then decrease further more slowly for higher Na coverages.

The W 4f XPS core-level spectra of WO$_3$ after Na dosing are reported in Figure 3b. The pristine WO$_3$ layer (bottom curve) displays two major core-level peaks due to the W 4f$_{7/2}$ and 4f$_{5/2}$ doublet emissions at $\sim$34.4 and $\sim$36.5 eV binding energy (BE), respectively. The WO$_3$ W 4f spectrum has been fitted with two core-level doublet components with W 4f$_{7/2}$ BEs of 34.4 eV (colored blue) and 35.1 eV (colored pink) due to the emission from W atoms located within the domains and at their edges, respectively (see ref 40 and Figure S2, Supporting Information for a more detailed discussion). At low Na coverages ($\Theta_{Na} = 0.2$ ML), the W 4f spectrum broadens slightly at the higher BE side, indicating that Na atoms adsorb initially near the domain boundaries. At a Na coverage of $\sim$0.3 ML, corresponding to the break of the slope in the $\Delta \Phi$ curve in Figure 3a, a new W 4f doublet evolves at the lower BE side (colored green) with a W 4f$_{7/2}$ BE of 33.6 eV.

On further Na dosing, the latter component gains in intensity at the expense of the pristine WO$_3$ components. At $\Theta_{Na} = 0.8$ ML, a distinct three-peak W 4f structure forms, consisting of two components with W 4f$_{7/2}$ BEs of 33.6 and 35.3 eV, which is reminiscent of W 4f spectra reported for Na$_x$WO$_3$ bronzes. The W 4f core-level shape at 1 ML broadens and shows less well-defined peaks: the Na$_x$WO$_3$-related peaks shift to somewhat higher binding energies of 34.1 and 36.1 eV, and an additional small W 4f$_{7/2}$ core-level component appears at the lower BE side, signaling some W species in a lower oxidation state. Figure 3c presents UPS spectra of WO$_3$/Pd(100) recorded after successive Na dosing. The pristine oxide surface (bottom curve) displays a narrow structure at the Fermi level $E_F$ (= 0 eV) due to emission from the Pd 4d states of the substrate and broader features at 2 and $\sim$4 eV, which are mainly oxide O 2p as well as Pd 4d derived. With increasing Na dosing, the intensity in the region 0 $\sim$3 eV below $E_F$ becomes slightly attenuated but remains essentially unchanged, whereas two new emission features emerge in the region 4.5 $\sim$9 eV, which shift progressively to the higher binding energy. After $\sim$0.8 ML Na dosing, two emission peaks are prominent at around 6 and 8 eV below $E_F$. These UPS observations are rationalized in conjunction with the partial DOS calculations presented below (Figure 5f).

Na 1s XPS (Figure 3d) and Na KLL Auger (Figure 3e) spectra were also measured as a function of Na coverage. At submonolayer Na coverages, the Na 1s and Na KLL spectra

Figure 3. (a) Work function change, $\Delta \Phi$, with respect to the pristine 2D WO$_3$ surface, as a function of the Na coverage. Two interaction regimes I and II are indicated. Inset: $\Delta \Phi$ as a function of Na coverage for 2D MoO$_3$. (b) W 4f spectra of the pristine 2D WO$_3$ layer on Pd(100) (bottom curve) and of the surfaces after dosing Na. The W 4f spectra are deconvoluted into different core-level components. (c) He I UPS spectra of the pristine WO$_3$ surface and after deposition of increasing Na coverages. The Na 1s core-level (d) and Na KLL Auger spectra (e) taken for different Na coverages. (f) Modified Auger parameters, plotted as a function of the Na coverage. The dashed lines indicate modified Auger parameter values for various Na-containing bulk compounds.
are peaked between 1071.2–1071.4 and 991.9–992.2 eV, respectively. With increasing the coverage between 1 and 2 ML, the Na Ls and Na KLL peak positions shift to 1072.2 and 989.7 eV, i.e., they converge to spectroscopic values characteristic of Na2O compounds. The modified Auger parameters of the surfaces dosed with Na plotted in Figure S3 are all within the range of ionic Na compounds, indicating that efficient charge transfer from the Na dopant atoms to the oxide host states has occurred. The detailed charge transfer paths will be addressed below in connection with the DFT calculations.

Based on the ΔΦ and XPS data, it is appropriate to distinguish two different sodium–oxide interaction regimes: the low-coverage regime I (ΘNa < 0.3 ML; ΔΦ < −2 eV) is associated with a doping behavior; in the high coverage regime II (ΘNa > 0.3 ML; ΔΦ > −2 eV) the chemical reaction of Na with the oxide layer leads to a destruction of the c(2×2) WO3/MoO3 structure and the formation of Na-bronze-like phases. In the following, the two interaction regimes will be investigated and discussed separately.

3.2.1. Doping Regime I. Na was dosed at room temperature onto the c(2×2) WO3/Pd(100) surface, and the evolution of the surface morphology and geometric structure with the Na coverage was monitored in STM. To image the Na atoms, the bias voltage U was set in the range between +2.0 and +3.0 eV, and the coverage was monitored in STM. To image the Na atoms, the surface morphology and geometric structure with the Na were investigated and discussed separately.

Initially, at 0.1 ML, Na atoms decorate the edges of the WO3 which corresponds to tunneling into the empty Na 3s states. The bias voltage U was set in the range between +2.0 and +3.0 eV, and the coverage was monitored in STM. To image the Na atoms, the surface morphology and geometric structure with the Na atoms was investigated and discussed separately.

The c(2×2) WO3 domain boundaries are clearly visible, but no new Na-related features can be distinguished here. The same behavior is also observed for the MoO3 monolayer surfaces at low Na coverages (Figure S5c,d, SI). It therefore appears that the Na interaction initially takes place preferentially at the c(2×2) domain boundaries.

At ΘNa ~ 0.3 ML, a (2×2) superstructure is recognized within the domains, as shown in the STM images in Figure 4c,d, which have been high-pass filtered for a better image contrast (the corresponding unprocessed images are reproduced in Figure S6, SI). The (2×2) order is limited only to a few unit cells and is therefore barely detectable in the LEED images. The domain boundaries are decorated with bright clusters with an apparent height of up to 3 Å, which without filtering would have dominated the image contrast. We can thus conclude that with increasing the coverage to 0.3 ML, Na atoms, besides condensing at the domain boundaries, also occupy fourfold hollow regular lattice sites inside the WO3 domains in the (2×2) superlattice. Above this critical Na coverage, the doping regime is terminated, as demonstrated in the STM images in Figure 4e,f, taken after the deposition of 0.4 ML. Here, the WO3 domain network is not visible anymore and the surface is partially covered by islands of nearly rectangular shape, whose edges are oriented along equivalent Pd[110] directions, i.e., they are rotated by 45° with respect to the c(2×2) WO3 domain boundaries. A closer look (Figure 4g) reveals that the rectangular islands display stripes running parallel to the Pd[011] direction, which are separated by a distance of 8.1 Å along the Pd[011] direction. We attribute these rectangular islands to a bronze-type 2D Na,WO3 phase forming as a result of the reaction of the WO3 monolayer with the Na atoms. This is confirmed by the XPS analysis (see Figure 3), which shows that this reaction is initiated already at room temperature, but due to kinetic limitations, well-ordered Na3WO3 phases cannot be grown. The latter requires temperature activation, and the formation of highly ordered 2D Na-bronze structures upon annealing at elevated temperatures are presented and discussed in the next section.

Figure 4. STM images of WO3 monolayer surfaces at different Na coverages: 0.1 ML (a,b), 0.3 ML (c,d), and 0.4 ML (e,f); (a) 50 nm × 50 nm (U = +2.0 V, I = 40 pA); (b) 20 nm × 20 nm (U = +1.5 V, I = 40 pA); (c) 50 nm × 50 nm (U = +3.1 V, I = 40 pA); and (d) 20 nm × 20 nm (U = +3.1 V, I = 40 pA). The images in (c) and (d) were high-pass filtered for a better contrast; (e) 100 nm × 100 nm (U = +3.0 V, I = 11 pA) and (f) 20 nm × 20 nm (U = +2.4 V, I = 32 pA).
DFT calculations of the Na\textsubscript{x}WO\textsubscript{3}/Pd(100) system were performed for several selected Na coverages in the doping regime, and the most stable structures found, and their adsorption energies and PDOS changes are displayed in Figure 5. For a single Na atom, the energetically most stable sites were found at the domain corners (see Figure 5a) with an adsorption energy of \(-1.08\) eV, followed by adsorption at the domain boundary, with an energy of \(\sim -0.81\) eV and eventually at the four-fold hollow sites within the domains, with an energy of \(\sim -0.3\) eV. A second Na atom is strongly repelled by the first one, increasing the energy of the system by \(+0.63\) eV when the Na atoms are first-neighbors (distance of \(\sim 2.7\) Å), and this repulsion decreases to \(+0.01\) eV at distances of \(\sim 7\) Å. Therefore, the very low-coverage regime consists of filling the domain boundaries with sparsely distributed Na atoms to minimize the Na–Na repulsion, up to 0.16 ML, where the most stable structure presents a domain boundary filled with Na atoms separated by a distance of 5.8 Å (see Figure 5b).

On further coverage increase, Na atoms may continue adsorbing at the domain boundaries, which increases the Na–Na repulsion, or start occupying the hollow sites within the domains. In both cases, the adsorption energy gain is similar and small, as shown in Figure 5e. Above 0.20 ML, Na adsorbs mostly within the domains (Figure 5c) and the total adsorption energy quickly reaches a minimum at around 0.35 ML (Figure 5d), where the weak energy gain due to Na adsorption is counterbalanced by the increased Na–Na repulsion. At this coverage, the WO\textsubscript{3} domains are fully covered by a p\((2 \times 2)\) Na adlayer, in line with the experimental observation (see STM images in Figure 4c,d). The same analysis performed for the MoO\textsubscript{3} system gives a similar picture, the main difference being the Na adsorption energy magnitude, which is lower by 0.15 eV per Na atom.

The triangular features observed in the STM images at low Na coverages (Figure 4a,b) can be understood by the DFT simulations. Focusing on the WO\textsubscript{3} system, we first found that Na adsorption at the domain boundaries reduces the oxygen vacancy formation energy by 0.10 to 0.20 eV, as demonstrated in Figure S4b (SI). A representative configuration is illustrated in Figure 6a, where two Na atoms are adsorbed at opposite domain boundaries, each of them inducing an oxygen vacancy.

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To balance this oxygen loss, the WO₃ domain boundaries reconstruct in a way shown in the model of Figure 6b, where pyramidal WO₄ units form at the domain boundaries. This reconstruction significantly reduces the total energy of the system by $-0.73$ eV. The simulated STM image (Figure 6c) reproduces very well the experimental STM contrast of the triangular features and thus supports our interpretation.

To rationalize the limiting Na coverage in the doping regime, we have also performed an analysis of the Na adsorption energy as a function of its coverage considering a simpler model: a continuous 2D WO₃ layer on Pd(100) without domain boundaries (Figure 7a). We found that Na adsorption is energetically favorable only up to a critical coverage of 0.25 ML (Figure 7b), which is due to the strong ionic bond between Na and its four closest oxygen atoms, that creates an inward oxygen displacement that shortens Na–O bonds by 8%. Since each Na atom is strongly bound to four oxygen atoms at 0.25 ML, any additional Na atoms will be unable to similarly bind to the surface without causing a large strain. This weaker binding, plus the increasing Na–Na repulsion, explains the instability at Na coverages higher than 0.25 ML. Therefore, the overall energetics of this system (Figure 7b) shows that Na adsorption is thermodynamically favorable up to 0.25 ML. As already discussed above, for the finite size WO₃ domains, Na first adsorbs in the boundaries, and after this within the domains. For this reason, the limiting Na doping coverage is somewhat higher (~0.35 ML), in close
agreement with the experimental findings. STM simulated images of the (2 × 2) Na adlayer are shown in Figure 7c and reveal that the Na atoms become visible only for bias voltages exceeding +2 V, as confirmed by the PDOS projected on Na atoms (Figure S7, SI).

The Lowdin charge analysis reveals that all Na atoms are in a Na⁺ state, with a positive charge of around +0.95 e⁻ per Na atom, in accordance with the XPS measurements (Figure 3d–f). The donated charge is transferred mostly to the closest O neighbors, especially the less coordinated ones, while the W atoms and the Pd substrate get only a small fraction of it. Other numerical approaches to evaluate atomic charge, namely, Bader and Voronoi, give similar qualitative results. The system’s work function presents a large and nearly linear decrease from 0 to 0.35 ML, dropping by −2.03/−1.86 eV for WO3/MoO3, respectively. This is in good quantitative agreement with the experimental results shown in Figure 3a. The changes in the PDOS as a function of the Na coverage are shown in Figure 5f, where three distinct Na-related peaks at −9, −7, and −4.5 eV evolve in the valence band, which shift to higher binding energies on increasing the Na coverage; this is in line with the observations in the experimental UPS spectra (Figure 3c).

3.2.2. Reaction Regime II. Annealing of Na-dosed WO3 surfaces with 0.4 ML < ΘNa < 1 ML in UHV to 673 K for 3 min causes the formation of various new ordered Na2WO3 phases. The work function generally increases on annealing, with higher Na coverages exhibiting a larger ΔΦ change, which varies between +0.8 eV at 0.4 ML and +1.4 eV at 1.0 ML. W 4f core-level XPS spectra taken after the annealing step (Figure S8a, SI) exhibit the characteristic “three-peak” spectral shape, typical for tungsten bronzes, whereas the corresponding Na 1s spectra (Figure S8b, SI) show only small narrowing due to the improved structural order. A collection of STM images of different Na2WO3 phases occurring in the Na coverage range 0.4 ML < ΘNa < 0.8 ML is presented in Figure S9 (SI). Briefly, between 0.4 and 0.6 ML, highly anisotropic Na-related islands are formed, displaying bright stripes running along equivalent Pd[011] directions. A DFT structure model for this stripe phase is proposed in Figure S10 (SI). At 0.8 ML, hexagonally shaped islands are grown, exhibiting an ordered hexagonal structure, which, however, coexists with other Na2WO3 phases.

Heating the 1 ML Na-dosed WO3 layer to 673 K generates only well-ordered hexagonal phases, as evidenced by the STM and LEED data presented in Figure 8. Large-area STM images (Figure 8a) display hexagonally shaped islands and a wetting layer covering the Pd(100) surface. The LEED pattern in Figure 9b consists of two concentric rings, each containing 12 reflections, which result from the diffraction from two equivalent orthogonal domains with a hexagonal structure. A closer look by STM (Figure 8c) reveals that both the wetting layer and the hexagonal islands exhibit a stripe structure with a periodicity of ~25 Å, with the stripes running parallel to the principal Pd[011] directions.

Obtaining stable STM images with atomic resolution over the timescale of one picture frame proved difficult, with the atomic contrast changing frequently. These changes are probably due to tip instabilities caused by occasionally picking up Na atoms from the Na2WO3 layer. The atomically resolved STM image in Figure 8b has been taken from the wetting layer and shows a well-ordered hexagonal lattice of a lattice constant of 5.0 ± 0.1 Å, with one of the unit cell vectors aligned with the Pd[011] direction. A line profile along one hexagonal row, as indicated in Figure 8d, is plotted in Figure 8e and shows a superposition of the atomic lattice corrugation and a wave with a periodicity of 25 Å due to the stripes (dashed lines). Obviously, the stripes correspond to a Moiré pattern, which is the result of a lattice coincidence of 5 hexagonal lattice constants with 9 Pd lattice constants (2.75 Å), which is equal to 24.8 Å and thus agrees perfectly with the stripe periodicity. High-resolution STM images taken from the hexagonal islands look very similar to that shown in Figure S7f and display a lattice constant of 5.0 ± 0.1 Å, i.e., equal to that of the wetting layer. It is interesting to note that the apparent height of the hexagonal islands shows a distinct bias dependence (Figure 8f): it varies between 2.5 Å at a bias of +1 V and increases steeply to 7 Å as the bias exceeds +3 V. We attribute this bias dependence to the different electronic structures of the hexagonal wetting layer and the hexagonal islands, as discussed in more detail below. In particular, the hexagonal islands are shown to exhibit a lower work function than the wetting layer, and as a consequence, the bias increases to values comparable to the work function, a dramatic increase of the tunneling current occurs due to tunneling into field emission.
resonance states.\textsuperscript{61} We note that a similar 2D hexagonal bronze phase forms on annealing of 1 ML Na on the MoO\textsubscript{3} monolayer on Pd(100), and LEED and STM results are presented in Figure S11a,b (SI).

The DFT calculations help in rationalizing the atomic structure of the hexagonal 2D Na\textsubscript{x}WO\textsubscript{3} phases formed in the reaction regime. First, a free-standing model of a 2D hexagonal WO\textsubscript{3} layer (Figure 9a, left) has been considered, whose structure is essentially different from that of a 2D cut of the hexagonal WO\textsubscript{3} bulk (3D) phase\textsuperscript{62} (Figure 9a, right): the six-membered WO\textsubscript{6} rings in the bulk structure are corner-linked, whereas in the 2D analogue they share edges. It has a lattice parameter of 5.13 Å, which is very close to that of the experimentally observed hexagonal Na\textsubscript{x}WO\textsubscript{3} phases (5.0 Å). Although such 2D hexagonal WO\textsubscript{3} phase could not be grown on the Pd(100) surface (probably due to unfavorable epitaxial conditions), it becomes stabilized in the presence of Na, as indeed experimentally observed. The DFT calculations show that Na atoms may adsorb at the positions of the hexagonal cavities on both sides of the 2D WO\textsubscript{3} layer, with saturation coverages of 0.5 and 1.0 ML (Figure 9b). The latter configurations are energetically more favorable than Na adsorption on the unsupported square WO\textsubscript{3} monolayer: the energy difference with respect to the square structure is a −0.004 eV/WO\textsubscript{3} unit at 0.5 ML and reaches −0.52 eV/WO\textsubscript{3} unit at 1 ML. This particular stability is mainly due to two factors: (i) a better lateral screening of the Na atoms due to the planar arrangement of the oxygen atoms in the hexagonal WO\textsubscript{3} monolayer, and (ii) the symmetry perpendicular to the plane, which allows two Na atoms to be adsorbed on each side with nearly equal adsorption energies. Thus, the hexagonal 2D WO\textsubscript{3} monolayer has the unique property to accommodate a three times larger load upon Na doping, forming a stoichiometric 2D Na\textsubscript{x}WO\textsubscript{3} layer at 1 ML, as compared with the bulk hexagonal WO\textsubscript{3} phase, where at a maximum 0.33 ML Na can be inserted in the hexagonal tunnels, resulting in bulk hexagonal Na\textsubscript{0.33}WO\textsubscript{3} bronzes.\textsuperscript{55}

The modeling of the hexagonal Na\textsubscript{0.5}WO\textsubscript{3} layers on the Pd(100) substrate with x = 0.5 and 1 was performed using the supercell detailed in Figure 9c. In both cases, the optimized geometry showed a well-preserved hexagonal symmetry and the corresponding simulated STM pictures (Figure 9d) reveal Moiré patterns due to the interaction with the Pd substrate, reproducing well the experimental images. The geometrical height of the NaWO\textsubscript{3} layer was found to be on average by 2 Å larger than that of the Na\textsubscript{0.3}WO\textsubscript{3} layer, which is in good agreement with the apparent height of the hexagonal islands with respect to the wetting layer at low sample bias (Figure 8f). The dramatic increase of the apparent height observed at higher bias voltages can be attributed to electronic effects. On the one hand, the calculated PDOS (Figure S11c, SI) shows that the NaWO\textsubscript{3} layer exhibits a significantly larger density of Na 3s-derived states at lower energies above the Fermi level than the Na\textsubscript{0.3}WO\textsubscript{3} layer. On the other hand, the calculated work function of the NaWO\textsubscript{3} layer is as low as 2.01 eV, which means that tunneling at bias voltages higher than this value may lead to a strong enhancement of the apparent height in the STM images due to tunneling into the image resonance states. All of these findings suggest that the hexagonal Na\textsubscript{0.3}WO\textsubscript{3} and NaWO\textsubscript{3} DFT-derived model structures are intimately related to the experimentally identified hexagonal wetting layer and second layer islands, respectively. The reason for the formation of a mixed Na\textsubscript{0.3}WO\textsubscript{3} and NaWO\textsubscript{3} film on Pd(100) at the nominal Na coverage of 1 ML is related to the fact that the latter coverage was referred to the surface density of the square WO\textsubscript{3} monolayer, which is by a factor of 1.4 smaller than that of the hexagonal WO\textsubscript{3} layer. Thus, to achieve a full coverage of the Pd(100) surface by the 2D NaWO\textsubscript{3} layer, both WO\textsubscript{3} and Na coverages have to be increased by this factor.

4. CONCLUSIONS

In summary, well-ordered 2D WO\textsubscript{3} and MoO\textsubscript{3} layers were epitaxially grown on Pd(100) to investigate the interaction of Na atoms with these oxide model phases using a combined experiment–theory approach. Depending on the Na concentration, we found two specific interaction regimes: (i) a doping regime, at low Na coverages, where the 2D WO\textsubscript{3} and MoO\textsubscript{3} lattices remain intact to a large extent upon Na adsorption and (ii) a reaction regime, at higher Na coverages, where new highly ordered 2D Na\textsubscript{x}WO\textsubscript{3} and Na\textsubscript{0.5}MoO\textsubscript{3} bronze-type phases form upon thermal activation. In the doping regime, Na atoms adsorb initially at the antiphase domain boundaries, causing their local reconstruction to balance the Na-induced oxygen loss. Subsequently, Na adsorbs in a (2 × 2) superlattice at the regular four-fold hollow terminal oxygen sites within the oxide domains. XPS measurements, supported by the Lowdin charge analysis, reveal that the Na atoms are almost fully ionized, donating their charge to the closest O neighbors. Above a critical Na coverage of ∼0.3 ML, the doping regime is terminated due to the strong elastic strain and electrostatic repulsion energy increase. This is in contrast to the 3D case, where the perovskite-type lattice is able to accommodate Na concentration up to x = 1, without major structural changes. The 2D lattices appear to be too flexible, on the one hand, and to provide less screening of adjacent Na charges, on the other hand. Thus, the original 2D oxide lattice becomes destroyed in the so-called reaction regime and new sodium bronze-type phases become stable. The most prominent one is the hexagonal phase, with a lattice constant of 5.0 Å, which can be considered as a 2D analogue of the bulk hexagonal Na\textsubscript{0.3}WO\textsubscript{3} structure. The structure of the 2D hexagonal phase has been understood in the DFT calculations and is based on a 2D hexagonal WO\textsubscript{3} layer, consisting of six-membered WO\textsubscript{6} rings, sharing edges. In the ring center, up to two Na atoms can be adsorbed on each side of the layer, resulting in two very stable 2D hexagonal bronze structures with formal stoichiometries of Na\textsubscript{0.1}WO\textsubscript{3} and NaWO\textsubscript{3}. The 2D confinement and the different polyhedral linkage with respect to their bulk counterpart, together with the higher concentration of sodium atoms, impart the 2D hexagonal Na\textsubscript{0.3}WO\textsubscript{3} and Na\textsubscript{0.5}WO\textsubscript{3} phases on Pd(100) with new and unforeseen physical and chemical properties to be further explored. The results of this study demonstrate that structurally well-defined 2D oxide systems may offer a suitable playground to model alkali doping phenomena in technologically relevant processes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c10696.

Work function measurement and Na coverage calibration; W 4f and Mo 3d XPS of c(2 × 2) WO\textsubscript{3}/MoO\textsubscript{3} on Pd(100); energy stability versus lattice parameter of free-standing WO\textsubscript{3}/MoO\textsubscript{3} layers; oxygen vacancy
formation energy for WO₃/MoO₃ layers on Pd(100); STM at low Na coverages on WO₃/MoO₃ layers on Pd(100); unprocessed STM images at 0.3 ML Na on WO₃ layers on Pd(100); Na PDOS; effect of annealing on W 4f and Na 1s XPS spectra of WO₃ layers on Pd(100); STM overview of Na,W₃O₇ phases formed in the reaction regime on Pd(100); DFT structure model of the stripe Na,W₃O₇ phase on Pd(100); LEED and STM of the hexagonal Na₂MoO₃ layer on Pd(100); PDOS of hexagonal Na₂WO₄ structures on Pd(100) (PDF)

![Image]

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**AUTHOR INFORMATION**

**Corresponding Authors**

Fabio R. Negreiros — INFIQC, CONICET, Departamento de Química Teórica y Computacional, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, 5000 Córdoba, Argentina; Email: fabian@cri.fcen.uba.ar

Svetlozar Surnev — Surface and Interface Physics, Institute of Physics, Karl-Franzens University, Graz A-8010, Austria; orcid.org/0000-0002-9756-0674; Email: svetlozar.surnev@uni-graz.at

**Authors**

Malíhe Mohammadi — Surface and Interface Physics, Institute of Physics, Karl-Franzens University, Graz A-8010, Austria

Thomas Radlinger — Institute of Electron Microscopy and Nanoanalysis, Graz University of Technology, Graz A-8010, Austria

Philip Edelmayer — Surface and Interface Physics, Institute of Physics, Karl-Franzens University, Graz A-8010, Austria

Falko P. Netzer — Surface and Interface Physics, Institute of Physics, Karl-Franzens University, Graz A-8010, Austria; orcid.org/0000-0001-5617-7225

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.1c10696

**Author Contributions**

This manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The DFT calculations performed in this work used computational resources from CCAD-Universidad Nacional de Córdoba (https://ccad.unc.edu.ar/) of SNCAD-MinCyT, Argentina, in particular Cluster Serafín, a part of the PAGE project (https://ccad.unc.edu.ar/equipamiento/cluster-serafin/).

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