# Growth and Characterization of Ultrathin $V_2O_v$ ( $y \approx 5$ ) Films on Au(111)

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The growth of vanadium oxide ultrathin films on Au(111) using physical vapor deposition of V and oxidation under 50 mbar of oxygen has been investigated with scanning tunneling microscopy, low-energy electron diffraction, X-ray photoelectron spectroscopy, and near-edge X-ray absorption fine structure analysis. Depending on the coverage, two different well-ordered coincidence monolayer structures with a V<sup> $\sim$ 5+</sup> oxidation state are observed. These arrangements do not correspond to any known bulk structures, and they are determined by the interaction between the oxide layer and the Au(111) surface, a finding that highlights the ability of vanadium oxides to adopt different structures. After completion of the first layer, a two-layer thick film which wets the substrate and has a surface structure similar to that of V<sub>6</sub>O<sub>13</sub>(001) is formed. This film does not exhibit a well-defined azimuthal orientation, which leads to ringlike structures in the low-energy electron diffraction pattern. The formation of the V<sub>6</sub>O<sub>13</sub>(001)-like film is shown to precede the nucleation and growth of V<sub>2</sub>O<sub>5</sub> islands start to grow as soon as the monolayer is completed.

## Introduction

Ultrathin metal oxide films are important for a wide range of technological applications. For instance, they play a crucial role in heterogeneous catalysis and in the protection of metals against corrosion.<sup>1</sup> Oxide layers with thicknesses in the nanometer range are also interesting on the fundamental scientific level because they may exhibit physical and chemical properties that considerably differ from those of the corresponding bulk materials.<sup>2,3</sup> This is due to their limited thickness (spatial confinement) and to the relative importance of their interface with adjacent materials. Thus, understanding the properties and the growth of oxide "nanolayers" is interesting and relevant to the development of novel materials and applications.

Vanadium oxides are an interesting class of materials since they exhibit a range of magnetic, electronic, and catalytic properties.<sup>4</sup> Vanadium has different stable formal oxidation states, and it is known that the conversion between vanadium oxides of different stoichiometries is rather easy. This property is one of the important factors that make vanadium oxides very good oxidation catalysts.<sup>4,5</sup> They are used for instance for the oxidation of SO<sub>2</sub> to SO<sub>3</sub> (an important step in the production of sulfuric acid) and for the selective oxidation of various hydrocarbons.4,6-8 In these applications, a small quantity of vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) is dispersed on the surface of a supporting oxide such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, or ZrO<sub>2</sub>. These systems are often referred to as "monolayer catalysts", <sup>6,9</sup> and depending on the support, they can have much higher reactivity and selectivity than  $V_2O_5$  alone.<sup>7,10</sup> Although it is rather clear that the supporting oxide plays an important role in influencing the electronic properties and the structure of the vanadium oxide layer, the physical origins of the improved catalytic properties are still not fully understood. Also, the exact nature (atomic structure, thickness) of the  $VO_x$  layers loosely called "monolayers" has still not been clearly elucidated. This was evidenced in a recent study, where it was shown that some of the common conclusions made on the structure of the layers based on frequency shifts observed with vibrational spectroscopy might be wrong.<sup>11</sup>

One of the factors hampering a more precise understanding of these systems is their considerable structural complexity. Vanadium oxide ultrathin films on single crystals represent model systems that can serve as tools to get some insight into the problems pertaining to the more complex technical catalysts. With respect to the use of oxide single crystals, growing the films on metal substrates provides the potential advantage that the resulting systems do not suffer from charging problems and thus can be more easily probed with electron-based surface science techniques.

Most of the previous model studies were carried out on vanadium oxide structures that were prepared in ultra-highvacuum (UHV)-compatible conditions (i.e., with oxygen partial pressures in the  $10^{-7}$ - $10^{-6}$  mbar range; see refs 12-15, for instance). The layers generally had a lower V oxidation state  $(V^{3+} \text{ to } V^{4+})^{12-15}$  as compared to those prepared at atmospheric pressure  $(V^{5+})$ .<sup>6,8</sup> In an attempt to increase the oxygen content of the deposited films, Wong et al. annealed their samples in O<sub>2</sub> pressures up to 10<sup>-3</sup> mbar in their UHV system.<sup>16</sup> Although the resulting films were mainly composed of V5+ cations (as determined by X-ray photoelectron spectroscopy (XPS)), they also contained a significant amount of V4+. According to published phase diagrams<sup>17,18</sup> at typical UHV pressures (even without oxygen pressure intentionally applied to oxidize vanadium),  $V_2O_5$  should be the most stable compound at room temperatures and also at temperatures 100 K above room temperature, which may be applied during vanadium oxidation. In a phase diagram published by Haber et al.<sup>5</sup> only data for temperatures above 500 °C are shown. However, extrapolating the curves linearly toward room temperature would lead to the

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conclusion that under UHV conditions V<sub>2</sub>O<sub>5</sub> should be the most stable compound at least at room temperature. In view of these results the presence of lower oxidation states in the vanadia layers prepared in the above-mentioned experiments may at least partly be assigned to kinetic effects, i.e., the limited speed of oxidation at low oxygen pressures. It may also play a role that in thermal equilibrium the oxide layers are expected to contain some defects at low oxygen pressure and high temperature. To overcome these problems, we decided to carry out the oxidation procedure at higher pressure using a purpose-built high-pressure cell. In the present paper, we report on the preparation of vanadium oxide ultrathin films on Au(111) by oxidation of vanadium under 50 mbar of oxygen. One of the reasons that motivated the use of Au(111) as a substrate is its inertness toward millibar pressures of oxygen (other metal surfaces could oxidize, reconstruct and form facets, etc). The structure and the composition of the resulting films have been investigated with scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), XPS, and near-edge X-ray absorption fine structure (NEXAFS) analysis.

### **Experimental Methods**

A part of the experiments was performed in a commercial UHV system with a base pressure  $< 1 \times 10^{-10}$  mbar (Omicron). This system contains facilities for sample preparation (sputtering, vanadium evaporation) and surface characterization. The analytical equipment includes a hemispherical electron analyzer and a dual-anode X-ray source for XPS, LEED optics, a quadrupole mass spectrometer, and a room temperature scanning tunneling microscope. NEXAFS experiments were carried out in another UHV system connected to the UE52-PGM undulator beamline of the BESSY II synchrotron radiation center in Berlin. This system contains standard sample cleaning/preparation equipment and had a base pressure of about 5  $\times$  10<sup>-10</sup> mbar during our experiments. In both systems, the sample could be heated radiatively from the backside with a tungsten filament. For temperatures higher than 400 °C, electron beam heating was applied by setting the sample to a positive high voltage (the W filament being at ground potential). The sample temperature was measured with a chromel/alumel thermocouple inserted and pressed into a slit on the side of the crystal. The sample holder, which consists of a small plate, some holding clamps, and two isolated thermocouple connectors, could be moved from the analysis/preparation chamber to the high-pressure cell with a dedicated transfer rod. The high-pressure cell was connected directly to the chamber via a gate valve, allowing sample transfer without exposure to the ambient atmosphere. The same sample holder, high-pressure cell, and transfer mechanism were used in both UHV chambers.

The Au(111) sample was cleaned by cycles of Ar<sup>+</sup> sputtering (4000 eV,  $\sim 7 \mu$ A) at room temperature and annealing at 700 °C for 20 min in UHV. This procedure was repeated several times until no contaminants were detected using XPS and extended terraces displaying the Au(111) herringbone reconstruction<sup>19</sup> could be observed with STM.

The films were grown by first evaporating a given quantity of metallic vanadium onto Au(111) in UHV and then transferring the sample in the high-pressure cell for the oxidation. Vanadium was evaporated from a rod (ChemPur, 99.9% V, 2 mm diameter) with an Omicron EFM3 electron beam evaporator. The Au(111) substrate was kept at room temperature during the evaporation. The evaporation rate was calibrated in situ with a quartz crystal microbalance (in both UHV systems) and from STM images taken after evaporation. The evaporation rate was typically  $\sim 0.4$  Å/min (0.2 monolayer equivalent (MLE)/min). The deposited V thicknesses are reported here in monolayer equivalents, where 1 MLE contains the same number of V atoms as one layer of Au(111) ( $\sim 1.39 \times 10^{15}$  atoms/cm<sup>2</sup>). After the V evaporation, the sample was moved to the high-pressure cell heating stage. The cell was then isolated from the rest of the UHV system and filled with 50 mbar of oxygen (99.999% purity, Linde). While the pressure was kept constant, an O<sub>2</sub> flow was established to avoid a pileup of contaminations originating from molecules desorbing from the heated surfaces. The sample was heated at 400 °C for 10 min using a halogen lamp. The temperature was then allowed to cool to about 100 °C before pumping down of the high-pressure cell and transfer of the sample back to the main chamber. Initial XPS experiments on thicker V films indicated that these oxidation conditions (pressure, temperature, and time) are sufficient to reach the full V<sup>5+</sup> oxidation state. One has to note that the whole high-pressure cell and transfer rod assembly are UHV-compatible and have been initially baked out and thoroughly degassed. After oxidation of the films, no traces of surface contaminations could be detected with XPS.

The XPS data were acquired using Mg Kα radiation (1253.6 eV). Spectra were recorded with an electron takeoff angle ( $\theta$ ) of either  $0^{\circ}$  or  $70^{\circ}$  with respect to the surface normal. The binding energy scale of the spectra was referenced to the Au4f7/2 peak of the clean Au(111) substrate at 84 eV.<sup>20</sup> No background intensity was subtracted from the spectra reported here. However, the spectra have been corrected for X-ray satellites using the routine supplied with the CasaXPS program.<sup>21</sup> STM images have been recorded at room temperature in the constant tunneling current mode. Commercial etched Pt/Ir tips (Molecular Imaging) have been used. The scanning x and y dimensions have been calibrated by imaging the unit cell of Au(111). To minimize the influence of X-ray- or e-beam-induced reduction processes, the films were always first probed with STM. XP spectra were acquired subsequently, and LEED patterns were recorded at the end of the analysis. NEXAFS spectra were recorded by sweeping the energy of the linearly polarized light between 510 and 540 eV while measuring the current flowing between the sample and ground potential (total electron yield) or monitoring the emitted electrons with a partial yield detector. Two different light incidence polar angles were used: 0° and 70°.

#### **Results and Discussion**

Figure 1a shows a  $100 \times 100 \text{ nm}^2 \text{ STM}$  image obtained after the deposition of about 0.26 MLE of V on Au(111) at room temperature. V islands periodically arranged in lines spaced by about 14 nm are seen on the surface. The spacing between the islands along the lines is on the average 7.2-7.5 nm. This arrangement corresponds to the periodicity of the well-known Au(111) herringbone reconstruction superlattice.<sup>19</sup> In the central part of the image, where the signal has been differentiated to enhance the contrast, one can indeed observe that the growing V islands mainly nucleate on the elbows of the herringbone reconstruction. These sites are situated at the boundary between two alternating domains of uniaxial contraction having a relative orientation of 120°. Within the domains, dislocation lines (seen as ridges in STM) arise from stacking transitions of the Au atoms induced by the contraction. The herringbone elbows are expected to be the most reactive sites at the surface of reconstructed Au(111), and the preferential nucleation of metals at these features was also previously reported for Ni and Mo, for instance.<sup>22-24</sup> Although it is known that V and Au can form



Figure 1. STM images of 0.26 MLE of V/Au(111): (a) as deposited at room temperature (100 nm  $\times$  100 nm, 0.5 V, 1 nA; middle part of the image differentiated), (b, c) after being annealed in 50 mbar of O<sub>2</sub> at 400 °C for 10 min ((b) 100 nm  $\times$  83.6 nm, 2 V, 0.2 nA, (c) 10 nm  $\times$  10 nm, 1.5 V, 0.2 nA).

bulk alloys,<sup>25</sup> no evidence such as the appearance of serrated steps points toward surface alloying for the deposition conditions used here. Indeed, the Au(111) terraces are still well-ordered after the deposition, and large-scale STM images (not shown) reveal that the Au(111) step edges remain straight and regular.

After the oxidation of the 0.26 MLE of V/Au(111) film at 400 °C, a disordered oxide monolayer covers a fraction of the substrate surface, as shown in Figure 1b. During the oxidation,

it appears that 2D mass transport of  $VO_x$  species occurs on the surface of Au(111) and extended oxide monolayer patches grow. This is in contrast to a situation where oxide islands would form at the initial position of the V clusters and remain on the elbows of the herringbone reconstruction. Closer inspection of the oxide film's structure (Figure 1c) allows the identification of several features, such as rings, zigzags, and brighter protrusions. However, it is obvious that the film has no long-range order. This is supported by the LEED results (not shown), where mainly the Au(111) spots are observed, along with some background intensity and very weak and diffuse spots. Subsequent annealing in UHV was necessary to order the film. Figure 2 displays STM images and a LEED pattern obtained after annealing of the film at 200 °C for 5 min in UHV. STM images (Figure 2a,b) show a rather well-ordered stripe structure, with a rectangular unit cell of about 3.6 Å  $\times$  15 Å (depicted as a gray rectangle in Figure 2b). The LEED pattern of the film is shown in Figure 2c, while in Figure 2d a reproduction of the LEED pattern using the unit cell identified from the STM images is superimposed on the recorded pattern (the substrate's 3-fold symmetry is taken into account for the LEED evaluation, and three rotational domains of the rectangular unit cell are used). It can be seen that the measured LEED pattern corresponds rather well to the 3.6 Å  $\times$  15 Å rectangular unit cell mentioned above. With respect to Au(111), which has a 2.884 Å hexagonal unit cell,<sup>26</sup> this vanadium oxide overlayer unit cell can be described by the matrix (0, 1.25 | 6, 3). In turn, that corresponds to a (0, 5 | 6, 3) coincidence lattice having a 14.4 Å  $\times$  15 Å Moiré unit cell. This Moiré pattern cannot be clearly distinguished in the STM image shown in Figure 2b; this might be due to a lack of resolution or to unfavorable tunneling conditions (bias, current). It is also possible that the Moiré pattern is not seen in the image because the interaction with the substrate is not strong enough. In that case, neighboring 3.6 Å  $\times$  15 Å unit cells of the oxide film would be structurally similar although the location of the substrate gold atoms below them is different. Careful inspection of Figure 2b reveals some periodic features within the 3.6 Å  $\times$  15 Å unit cell. However, modeling the atomic structure within the unit cell would require better resolved images and the support of theoretical calculations (perhaps in combination with vibrational spectroscopy data). The observation that the films are disordered after their preparation at 400 °C in 50 mbar of O2 and that they get ordered after being annealed at lower temperature (200 °C) in UHV is noteworthy. This indicates that the ordering processes occurring in 50 mbar of O2 and under UHV conditions are different and that the oxygen pressure plays an important role. A small oxygen loss during the UHV annealing would probably be enough to allow the thermally induced rearrangement of supported  $VO_x$ units from ring and zigzag structures into a more extended ordered layer. However, the oxygen loss during UHV annealing up to 200 °C must be rather small since the XPS O/V ratio and the V2p binding energy remain very similar before and after the UHV annealing procedure. Another possible explanation would be that the film could already lose a bit of oxygen at the end of the oxidation procedure, when the high-pressure cell is pumped down while the sample temperature is still around 100 °C. In other words, a structure with higher oxidation state could exist in 50 mbar of O<sub>2</sub> but become unstable and lose oxygen during the transfer to UHV. The resulting reduced layer would then form an ordered structure if enough thermal energy were supplied to overcome the activation energy barrier for the ordering process (here, after being annealed to 200 °C). In any case, the oxygen loss must be rather small since, as will be



**Figure 2.** STM images ((a) 50 nm  $\times$  50 nm, 2.5 V, 0.2 nA, (b) 10 nm  $\times$  10 nm, 2.5 V, 0.2 nA) and LEED pattern (c) obtained after annealing of a film formed by the oxidation of 0.26 MLE of V/Au(111) (see Figure 1). (d) Reproduction of the LEED pattern using a 3.6 Å  $\times$  15 Å rectangular unit cell and taking into account the substrate 3-fold symmetry (the bright spots at the border of the screen are the Au(111) (10) spots).>

shown below, the V atoms in the ordered film still have an oxidation state very close to 5+ (the highest oxidation state of vanadium).

For higher coverage of the first vanadium oxide layer, another ordered structure has been identified. Figure 3 shows STM and LEED data corresponding to a film obtained by the oxidation of 0.52 MLE of V/Au(111), followed by annealing in UHV at 200 °C for 5 min (to order the film). This coverage corresponds approximately to the formation of a full monolayer of the oxide. This is substantiated by the fact that large-scale STM images (not shown) did not reveal any bare Au(111) patches and at the same time displayed only step heights equivalent to those characteristic of the underlying Au(111) substrate. Correspondingly, the LEED Au(111) reflexes are much weaker (compare Figure 2c,d to Figure 3b,c). As seen from the STM picture shown in Figure 3a, two different structures coexist in the layer: "broader" stripes that are spaced by about 15 Å or appear as isolated features and "thinner" lines having a periodicity of 9 Å. The second structure seems to be predominant. Although no atomically resolved STM images could be obtained for this film, it is tempting to assign the first structure to the one observed at lower coverage (with a 3.6 Å  $\times$  15 Å rectangular unit cell). Indeed, the lines observed in STM are spaced by 15 Å, and a good fraction of the measured LEED diffraction spots are reproduced using this structure. The rest of the spots can be accounted for by using an additional structure having a (1.25 × 3.75) unit cell with respect to the substrate. This structure has a 3.6 Å × 10.8 Å ( $\alpha = 60^{\circ}$ ) oblique unit cell. As depicted in Figure 3d, the vertical distance between the two short sides of this oblique lattice is equal to 9 Å, in very good agreement with the distance measured between the thinner lines observed with STM (assuming that the short unit cell vector is aligned along the lines). This structure also forms a (5 × 15) coincidence lattice, i.e., a 14.4 Å × 43.3 Å oblique Moiré net. It is possible that this explains some faint LEED spots that were not accounted for in Figure 3c.

The  $(1.25 \times 3.75)$  structure is predominant for coverages approaching a complete monolayer, whereas it was not observed at low coverage (see Figure 2). It is thus probably a more compact structure than the one having a 3.6 Å × 15 Å rectangular unit cell. Interestingly, both unit cells share a common short vector length of 3.6 Å. This value is very similar to the one found along the [010] direction of V<sub>6</sub>O<sub>13</sub> and V<sub>2</sub>O<sub>5</sub> (respectively 3.68 and 3.56 Å),<sup>27–29</sup> where it corresponds to the distance between adjacent corner-sharing distorted VO<sub>6</sub> octahedra or, in the case of a single layer, corner-sharing distorted VO<sub>5</sub> square pyramids. By analogy to the case of vanadium oxide monolayers on Rh(111),<sup>30</sup> it is very possible that the monolayer



**Figure 3.** STM image (a) (40 nm × 40 nm, 2 V, 0.2 nA) and LEED pattern (b) of a film formed by the oxidation of 0.52 MLE of V/Au(111). (c) Reproduction of the LEED pattern using 3.6 Å × 15 Å rectangular and 3.6 Å × 10.8 Å ( $\alpha = 60^{\circ}$ ) oblique unit cells (green and orange spots, respectively). (d) Real space arrangement of the 3.6 Å × 10.8 Å ( $\alpha = 60^{\circ}$ ) oblique unit cells forming the rows spaced by 9 Å observed in STM. Some contrast lines corresponding to the two different structures are indicated in (a).

films observed here on Au(111) are composed of VO<sub>5</sub> square pyramid building blocks that are sharing corners and edges at their base. Depending on the coverage and on the precise oxygen content, different arrangements of these units resulting in more or less compact structures are then possible. The facile rearrangement of coordination polyhedra in vanadium oxides is wellknown. It is involved, for instance, in the series of shear-plane transitions occurring during the reduction of bulk  $V_2O_5$  (to  $V_6O_{13}$ , for example).<sup>5</sup> The hypothesis that the films might be composed of VO<sub>5</sub> pyramids, a feature characteristic of  $V_2O_5$ , is also supported by the fact that the oxidation state of the V cations in these films is close to 5+. This is revealed by the V2p and O1s XPS data shown in Figure 4. Before discussion of these data, it is perhaps noteworthy to mention that the evaluation of vanadium oxidation states based on the XPS V2p and O1s peak intensity ratio is known to be rather complex and sometimes somewhat subjective.<sup>31,32</sup> This is for several reasons. First, because of a strong hybridization between V3d and O2p levels, the V2p signals have satellites at higher binding energy which are partially convoluted with the O1s peak.<sup>33</sup> Depending on the oxidation state, the position of these satellites can vary such that it is often very difficult to take them into account correctly. Further problems include the choice of an appropriate background subtraction and the possible presence of O1s shakeup satellites.<sup>32</sup> For these reasons, the position of the  $V2p_{3/2}$  signal (which shifts from  ${\sim}512.4$  eV for  $V^{0+}$  to  $\sim$ 517.2 eV for V<sup>5+ 34</sup>) is normally used instead of the V2p/ O1s ratio to identify V oxidation states. We have used this approach to interpret the spectra shown in Figure 4. One can see in this graph that some changes in the peak positions occur as a function of the film thickness. As will be shown in a forthcoming paper,<sup>35</sup> the oxidation of thicker V films (spectrum d) results in the growth of  $V_2O_5(001)$  and indeed the  $V2p_{3/2}$ signal of such layers has a binding energy of 517.15 eV. This value is similar to the ones reported in the literature for bulk  $V_2O_5$ .<sup>31,34,36,37</sup> In the case of the monolayer films (spectra a and b), the  $V2p_{3/2}$  signal has a binding energy of about 516.5 eV, which would normally be attributed to a slightly lower oxidation state (of stoichiometry between those of  $VO_2$  and  $V_2O_5$ ). However, this is not necessarily the case since for thin layers the XPS final state core holes may be effectively screened by the Au(111) substrate electrons, an effect that would also lead to a reduced binding energy as compared to that of the thick film case. The observation that the V2p and O1s levels are shifted by about the same energy into the same direction may be viewed as an indication that the shift is mainly a final state effect since the O1s binding energy usually depends only weakly on the oxidation state.34,36 Similar final state effects were observed for Nb<sub>2</sub>O<sub>5</sub>/Cu<sub>3</sub>Au(100),<sup>38</sup> V<sub>x</sub>O<sub>y</sub>/Rh(111),<sup>30</sup> and V<sub>2</sub>O<sub>3</sub>/  $Pd(111)^{39}$  monolayer films. Still, the discussion on the ordering



**Figure 4.** XP spectra (V2p and O1s region,  $\theta = 70^{\circ}$ ) of V<sub>x</sub>O<sub>y</sub>/Au(111) as a function of the V coverage initially deposited: (a) 0.26 MLE, (b) 0.52 MLE, (c) 1.04 MLE, (d) 7.8 MLE. In all cases, the intensity was normalized to the background signal at 500 eV (the spectra were afterward shifted with respect to each other along the *y* axis for display).

of the films in UHV at 200 °C (see above) showed that it is probable that the vanadium atoms do not have the highest oxidation state possible (5+). One can thus conclude that the average V oxidation state in the monolayer films is 5+ or slightly below. As mentioned before, the layers might be composed of VO<sub>5</sub> square pyramid building blocks that share corners and edges at their base. The stoichiometry of the layer will vary to a small extent depending on how these building blocks are connected: the oxygen content will be higher if the square pyramids rather share corners, and it will be lower when edges are shared. For instance, in the case of V2O5 each pyramid shares two edges and one corner in the (001) plane (see Figure 11).<sup>28,29</sup> It is possible that some of the VO<sub>5</sub> square pyramids composing the monolayer structures observed here share a higher number of edges, resulting in an overall stoichiometry slightly below that of  $V_2O_5$ .

The  $(1.25 \times 3.75)$  monolayer film obtained after the oxidation of 0.52 MLE of V/Au(111) has also been investigated with angle-resolved NEXAFS. In addition to information about the electronic structure of the materials, this technique also gives insight into the geometry of the interatomic binding. Indeed, the transition matrix elements determining the NEXAFS absorption intensity are connected to the polarization of the exciting beam and the orientation of the molecular bonds. The film has been probed with two different incidence polar angles ( $\alpha$ ) of the polarized light,  $70^{\circ}$  and  $0^{\circ}$ , and the resulting spectra are shown in Figure 5. The features situated between 515 and 529 eV are related to excitations from the V2p core levels into unoccupied or partially empty V3d orbitals, whereas the peaks in the 529-535 eV region pertain to the O K edge and correspond to transitions from O1s levels to O2p states mixed with V3d levels in the conduction band (O1s  $\rightarrow$  O2p + V3d).<sup>33,40,41</sup> The O K absorption spectrum also contains some features between 537 and 550 eV that are associated with O1s  $\rightarrow$  O2p + V4sp excitations, but these will not be discussed here. In a first approximation, the two broad structures centered at  ${\sim}519$  and 525 eV can be assigned to the vanadium  $L_{III}$  edge



**Figure 5.** NEXAFS spectra of a film formed by the oxidation of about 0.7 ML of V/Au(111). The spectra were acquired at two different light incidence angles ( $\alpha$ ): 0° and 70°.

 $(V2p_{3/2})$  and  $L_{II}$  edge  $(V2p_{1/2})$ , respectively. The precise shape of the spectra is determined by intra-atomic electronic interactions, dipole selection rules, and the structure of the unoccupied states above the Fermi level. In fact, it has been shown that both the transition energy and the line shape of the V L edge vary markedly for different vanadium oxides. According to the results published by Chen et al., the position of the V L<sub>III</sub> edge shifts from 515.5 eV for metallic V to 519 eV for V2O5, with a linear increase of about 0.7 eV per oxidation state.<sup>42</sup> In Figure 5, the V L<sub>III</sub> edge is centered at a transition energy of about 519 eV, an observation which supports the conclusion that the V oxidation state in the monolayer film is close to 5+ (final state screening effects play a smaller role in the excitation of intramolecular electronic transitions than they do in photoemission processes<sup>40</sup>). However, the shape of the V edge somewhat differs from the one observed in the spectra of  $V_2O_5(001)$  single crystals (see Figure 6). This is not surprising, and it confirms that the structure of the film does not fully correspond to regular  $V_2O_5$ . On the other hand, many spectral features are similar, perhaps indicating that the monolayer film and V2O5 have some common structural elements. For instance, the angular dependence of the O K edge between 529 and 535 eV is rather well reproduced. This region is composed of two peaks due to the crystal field splitting of the V3d bands.33,41 The sharp band observed at lower energy corresponds to transitions to t2g-type vanadium levels (pointing between O ligands, forming weaker  $\pi$  antibonding combinations with O2p orbitals) and the upper broad band to eg-type levels (oriented toward the ligands, forming stronger  $\sigma$  antibonding combinations with O2p orbitals). In the case of V<sub>2</sub>O<sub>5</sub>, calculations made by Kolczewski et al. showed that the lower energy peak is determined mainly by the oxygen atoms of the vanadyl groups (V=O).43,44 This peak is most intense if the electric field vector of the X-rays is perpendicular to the V=O bonds (normal light incidence in Figure 6,  $\alpha = 0^{\circ}$ ), and it becomes less intense than the upper band when the E vector becomes parallel to them (grazing incidence in our case,  $\alpha = 70^{\circ}$ ). The close reproduction of the features found for V<sub>2</sub>O<sub>5</sub>(001) in the NEXAFS spectra of the



**Figure 6.** NEXAFS spectra of a V<sub>2</sub>O<sub>5</sub>(001) single crystal cleaved in UHV. The spectra were acquired at two different light incidence angles ( $\alpha$ ): 0° and 70°

thin layer as shown in Figure 5 may be viewed as a hint that the thin layer and  $V_2O_5(001)$  contain similar structural elements including vanadyl groups pointing along the surface normal. In the case of  $V_2O_5(001)$  these are responsible for a significant part of the angle-dependent intensity in the O K region. This would support the idea of a film composed of VO<sub>5</sub> square pyramids sharing edges or corners of their base at the interface and exposing apical vanadyl O atoms at the surface as also proposed by Schoiswohl et al. for vanadium oxide monolayers on Rh(111).<sup>30</sup> However, as mentioned above, the details of the NEXAFS spectra depend on many factors and the support of calculations would be necessary to ascertain this model.

Neither of the two monolayer structures could be assigned to a known bulk vanadium oxide structure. They are coincidence structures, which points toward a certain degree of interaction with the substrate. The stabilization of unusual oxide structures by metal surfaces is a rather well-known phenomenon.<sup>3</sup> For films having a thickness of only a few atomic layers, the proximity to the metal surface perturbs the electronic structure of the oxide, leading to atomic arrangements specific to the interface. Although Au(111) might be expected to be rather unreactive, it has been shown before that it can stabilize special interfacial oxide structures: in the case of MoO<sub>3</sub>, which has a bulk *bilayer* structure, an epitaxial  $c(2 \times 4)$  MoO<sub>3</sub> monolayer has been obtained on Au(111).45,46 Density functional theory predicted that the MoO<sub>3</sub> monolayer induces an electronic charge redistribution above the Au surface, thereby satisfying the local Mo bonding requirements and stabilizing the oxide film.<sup>47</sup>

Figure 7 shows STM images and a LEED pattern obtained after the oxidation of 1.04 MLE of V/Au(111), followed by annealing in UHV at 200 °C for 5 min. The amount of deposited V is twice the quantity used in the case of the second monolayer film described above (see Figure 3), where about a full monolayer was obtained. The large-scale STM image displayed in Figure 7a shows that the film's topography is still very flat, with steps separating rather large terraces. Atomic resolution STM images (Figures 7b and 8) reveal a structure composed of double rows with neighboring double rows shifted by 50% of the repeat distance within the rows with respect to each other (along the direction of the rows). This corresponds to a 3.6 Å  $\times$  6 Å,  $\alpha = 73^{\circ}$ , oblique surface unit cell as depicted by a gray parallelogram in Figure 7b. This unit cell has been successfully used to reproduce the measured LEED pattern of the film, as shown in Figure 7c,d. One can also observe that rings connect the LEED spots, which will be discussed later.

A closer view of the surface structure observed with STM is given in Figure 8a, where the unit cell is indicated by a dotted parallelogram. This image corresponds rather well to the pictures obtained by Smith et al. on a cleaved V<sub>6</sub>O<sub>13</sub>(001) single crystal.<sup>48</sup> These authors also reported some calculated partial electron density contour plots for different V<sub>6</sub>O<sub>13</sub>(001) surfaces (obtained for various cleavage planes perpendicular to the [001] direction). To a first approximation such contour plots describe the contrast observed in STM images.<sup>49</sup> Figure 8b shows a projected view of the V<sub>6</sub>O<sub>13</sub> crystal structure along [010], while Figure 8c displays the (001) surface obtained after cleavage along the red line shown in Figure 8b. Smith and co-workers have determined that this cleavage plane is the most favorable for  $V_6O_{13}(001)$ and that the resulting surface does not significantly relax. The contour plot calculated for this surface in ref 48 corresponds well to the STM image shown in Figure 8a. The origin of the contrast difference between the two sides of the double rows probably stems from the fact that V<sub>6</sub>O<sub>13</sub> is a mixed-valence compound. On the basis of the different V-O bond lengths in the crystal, Wilhelmi et al. estimated that some V cations have an oxidation state close to 5+, while others are closer to 4+.<sup>27</sup> In the surface plane depicted in Figure 8c, two different cation sites coexist according to their prediction: the ones marked by an asterisk should be the closest to 5+, and the others have a slightly lower oxidation state (the two sites are characterized by slightly different V–O bond distances). Each cation type occupies one side of the V double rows, and it is near at hand to attribute the observation of V rows with different intensities in Figure 8a to this oxidation state difference. Recently, almost identical STM images have also been obtained for V<sub>6</sub>O<sub>13</sub>(001) thin films produced at the surface of reduced  $V_2O_5(001)$  single crystals.50

The V2p and O1s XP spectrum obtained for this film is shown in Figure 4c. Compared to the spectra of the monolayer films (spectra a and b), it is noteworthy that the core levels are shifted toward higher binding energy. This indicates that the possible screening effects described earlier are effectively limited to the first oxide layer. The maximum of the V2p<sub>3/2</sub> peak is now situated at a binding energy of about 517.1 eV. This value is very close to the one typical for V<sub>2</sub>O<sub>5</sub> and deviates from the one obtained for V<sub>6</sub>O<sub>13</sub> bulk samples (516.5 eV).<sup>31,37</sup> However, it is clear that the peak is broadened toward lower binding energies. Part of this effect can be explained if the film indeed has a mixed-valence character. Additional broadening of the peaks may be due to the presence of a shoulder at lower binding energy, which could arise from the detection of photoelectrons originating from the first (screened) layer. As shown in Figure 9b, this is supported by the fact that the shoulder becomes more intense with respect to the main peak when less surface sensitive XPS conditions are employed (i.e., when the photoelectrons are collected normal to the surface,  $\theta = 0^{\circ}$ ). In Figure 9, angledependent XPS spectra corresponding to a monolayer film (oxidation of 0.52 MLE of V) are also displayed for comparison (spectra a). In this case, the shape of the V2p peaks remains similar for both takeoff angles ( $\theta$ ).

We note that the bulk unit cell of  $V_6O_{13}$  along [001] contains three layers (see Figure 8b), whereas the thin film is only two



Figure 7. STM images ((a) 100 nm × 100 nm, 2 V, 0.2 nA, (b) 10 nm × 10 nm, 2 V, 0.2 nA) and LEED pattern (c) of a film formed by the oxidation of 1.04 MLE of V/Au(111). (d) Reproduction of the LEED pattern using a 3.6 Å × 6 Å,  $\alpha = 73^{\circ}$ , oblique unit cell.

layers thick. In that sense, the film is probably better described as "V<sub>6</sub>O<sub>13</sub>(001)-like". In this context, it has to be mentioned that the unit cell measured here (determined from LEED), 3.6 Å × 6 Å, is slightly compressed with respect to the surface unit cell of V<sub>6</sub>O<sub>13</sub>(001), which is 3.68 Å × 6.26 Å.<sup>27</sup> It is also clear that, although there is a very good agreement between our STM images and the data measured/calculated by other authors, a completely unambiguous determination of the surface structure cannot be made at the moment. In that respect, it is not very surprising that the value of the V2p<sub>3/2</sub> core level binding energy is different (by about 0.6 eV) for this ultrathin film and bulk V<sub>6</sub>O<sub>13</sub> samples. On the other hand, very few studies have been reported for V<sub>6</sub>O<sub>13</sub> surfaces, and in most cases the surface preparation of the samples along with possible effects such as relaxation or reconstruction remain poorly documented.

As mentioned previously, the LEED pattern of this film shows rings connecting the diffraction spots. This means that the various domains in the V<sub>6</sub>O<sub>13</sub>(001)-like film have somewhat random azimuthal orientations. However, as judged from the diffraction pattern it is clear that there is still a preferential orientation along the substrate's main crystallographic directions. It also seems that the azimuthal disorder is *slightly* smaller when the oxidation is carried out at higher temperatures (~500-550 °C, not shown here). The presence of azimuthal disorder probably stems from a rather weak interaction between the film and the substrate. During oxidation domains might grow rapidly in directions that depend only weakly on the interaction with the substrate since the interaction energy is expected to be small and likely does not depend very much on the azimuthal angle. As the domains get more extended, the thermal energy required to reorient them will increase. This is in contrast to the case of the monolayer films described previously, where the oxide structure is most likely determined and stabilized by the interaction between the film and the substrate.

The structure of the films has also been investigated for higher thicknesses. Figure 10 displays STM images obtained for a film prepared by the oxidation of about 1.56 MLE of V/Au(111), a thickness slightly larger than ( $\sim 1.5$  times) the one required for the formation of the  $V_6O_{13}(001)$ -like thin film described above. The images have been differentiated to allow the visualization of the various topographic features without contrast saturation. It appears that some crystallites have grown on top of another oxide layer. Smaller scale images (not shown here) revealed that the layer between the crystallites has the same surface structure as the  $V_6O_{13}(001)$ -like thin film. In the case of the crystallites, however, the distance between the bright contrast rows is ~11.5 Å, a value typical for V<sub>2</sub>O<sub>5</sub>(001) surfaces.<sup>48</sup> It thus seems that the  $V_6O_{13}(001)$ -like film acts as an interface layer between the Au(111) substrate and a growing  $V_2O_5(001)$ film. The crystalline structure of V<sub>2</sub>O<sub>5</sub> projected along [010] is depicted in Figure 11a. V<sub>2</sub>O<sub>5</sub> has an orthorhombic structure consisting of layers parallel to (001).<sup>5,28,29</sup> The V coordination



**Figure 8.** (a) STM image (3.4 nm  $\times$  3.4 nm, 2 V, 0.2 nA) of a film formed by the oxidation of 1.04 MLE of V/Au(111). (b) V<sub>6</sub>O<sub>13</sub> crystal structure projected along [010]. (c) (001) surface obtained after cleavage of a V<sub>6</sub>O<sub>13</sub> crystal along the plane indicated by a red line in (b). Unit cells are indicated by dotted lines. Blue and gray spheres correspond to O and V atoms, respectively

is best described as distorted square pyramidal, and the layers are composed of VO5 units that are sharing edges or corners in the (001) plane. For each square pyramid, the apical oxygen atom forms a double bond with the V atom, and these vanadyl groups are oriented along [001] in alternating directions toward one of the next neighboring layers. The layers are considered to be held together by van der Waals V=O····V interactions. The arrangement of  $V_2O_5(001)$  is shown in Figure 11b, where double rows of vanadyl O atoms are seen to extend along the [010] direction. This surface has a 3.56 Å  $\times$  11.52 Å rectangular unit cell. Careful inspection of the V<sub>2</sub>O<sub>5</sub>(001) islands reveals that they grow with a preferential orientation with respect to the underlying interface. Indeed, the double-row structures of the interface and the growing crystallites are generally aligned parallel to each other. This is shown in Figure 10b, where arrows indicate the [010] direction (along the double rows) of the different domains. The relative orientation of the two layers would correspond to a rather favorable epitaxial relationship. For the V<sub>6</sub>O<sub>13</sub>(001)-like surface, a 3.6 Å  $\times$  11.45 Å rectangular



**Figure 9.** XP spectra (V2p and O1s region) of films formed by the oxidation of (a) 0.52 MLE of V/Au(111) and (b) 1.04 MLE of V/Au(111). The spectra were acquired with two different electron takeoff angles ( $\theta$ ): 0° and 70°. The intensity was normalized to the background signal at 500 eV for each film (the sets of spectra a and b are however shifted along the intensity scale with respect to each other).



**Figure 10.** STM images ((a) 100 nm  $\times$  100 nm, 3 V, 0.2 nA, (b) 44 nm  $\times$  20 nm, 3 V, 0.2 nA) of a film formed by the oxidation of 1.56 MLE of V/Au(111) (differentiated images). In (b), arrows indicate the [010] direction of the various domains (see the text).

unit cell can be drawn by using the short unit vector of the primitive oblique unit cell and considering a longer unit vector going from one double row to the second nearest double row (which is not shifted with respect to the first one). A rather small misfit between the two layers can then be obtained for a parallel alignment of the double rows. Although this seems reasonable, the present data do not allow to exclude the possibility that the  $V_2O_5$  crystallites extend to the Au(111) surface and that the  $V_6O_{13}$ -like structure would not subsist at the interface. In Figure 10, it can also be observed that the crystallites have an elongated



**Figure 11.**  $V_2O_5$  crystal structure: (a) projected along [010] and (b) (001) surface. Unit cells are indicated by dotted lines. Blue and gray spheres correspond to O and V atoms, respectively. The vanadyl O atoms are represented by light blue spheres

shape and that they seem to grow more favorably along their [010] direction (along the vanadyl double rows). This preferential growth direction appears to be typical for V<sub>2</sub>O<sub>5</sub>; it was also found by Groult and co-workers, who observed the formation of [010]-elongated nanocrystals (with AFM and XRD) after annealing amorphous vanadium pentoxide thin films on silicon in air.<sup>51</sup> V<sub>2</sub>O<sub>5</sub> single crystals prepared by melt techniques are also known to be generally more extended in the [010] direction.<sup>52</sup> Upon further growth (i.e., if a thicker V layer is oxidized), flat V<sub>2</sub>O<sub>5</sub>(001) films containing a low number of point defects can be obtained. This is reported in a separate paper (ref 35).

#### Conclusions

In this work, we have shown that vanadium oxide monolayer structures with a  $V^{\sim 5+}$  oxidation state can be formed on Au(111) by oxidation of vanadium in 50 mbar of O2. Two well-ordered coincidence layers that do not correspond to any known bulk structures have been observed. These results evidence the fact that, due to the easy rearrangement of VO5 units in vanadium( $\sim$ 5+) oxides, a complicated range of interface-mediated monolayer structures can be obtained. It can be predicted that monolayers forming on other substrates such as  $SiO_2$ ,  $Al_2O_3$ , TiO<sub>2</sub>, etc. under similar preparation conditions will adopt rather different structures for every substrate. This goes along with the recent findings of Gao et al., who investigated the growth of vanadium oxide on the (101) and (001) surfaces of anatase.<sup>53,54</sup> On the two surfaces, they have obtained different epitaxial vanadium( $\sim$ 5+) oxide monolayers. Obviously, the structural dependence of vanadium oxide monolayers on the supporting material should be taken into account when, for instance, the reactivity of thin films supported on various oxides is compared.

The results also show that a two-layer-thick wetting film having a structure different from that of bulk  $V_2O_5$  can be grown under preparation conditions (temperature,  $O_2$  pressure) suitable for the formation of  $V_2O_5$ . This finding is rather interesting because it is in contrast with a rather generally accepted idea in the catalysis literature, where  $V_2O_5$  crystallites are often

assumed to start forming as soon as a monolayer is completed.<sup>6</sup> The onset of  $V_2O_5$  crystallite formation as a function of loading is often detected with Raman spectroscopy (monitoring bands pertaining to crystalline  $V_2O_5$ ), and the result is used to calculate the monolayer coverage in  $VO_x$  units/nm<sup>2</sup>. Doing so, the possibility that thicker films might form before  $V_2O_5$  crystallizes is disregarded. Our results suggest that such analyses should be considered with more caution.

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