First-principles calculations for \( V_xO_y \) grown on Pd(1 1 1)

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Abstract

An approach to access the stability of oxides growing on top of a metal support is presented. In combination with first-principles calculations, it allows to predict the stable structures as a function of the thickness of the evaporated metal ad-layer and as a function of the oxygen pressure. The ideas are applied to thin vanadium oxide films growing on Pd(1 1 1). To investigate the stability of these oxide films, first-principles calculations for more than 50 thin films of \( V_xO_y \) on Pd were performed at varying stoichiometry and coverage. The general principles determining the growth of thin vanadium oxide films on Pd(1 1 1) are discussed, and the experimental results are interpreted in the light of the first-principles calculations. At 1 ML vanadium coverage, a complicated succession of structures is predicted by the calculations. At high oxygen pressure bulk like \( V_2O_3 \) phases are stable. At lower oxygen pressure, however, a surface stabilised \((2 \times 2)\) reconstruction with a formal stoichiometry of \( V_2O_3 \) is predicted, and rectangular and hexagonal vanadium-dioxide phases are expected to grow. At very low oxygen pressures, first the vanadium-dioxide phases and then the surface \( V_2O_3 \) phase decompose and the liberated V atoms move subsurface. These predictions are in good general agreement with experiment. An important result of the study is that the metal surface stabilises thin films which have no equivalent bulk phases. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The growth of thin oxide films on a metal support is a fascinating field of surface science which has recently gained substantial attention. The interest partly stems from the technological importance of thin oxide films, but also from a fundamental point of view these materials are a challenge. It is unclear to which extent the physical, chemical and structural properties of thin films differ from those of bulk materials, and how growth and morphology are affected by the metal support [1–4]. The experimental characterisation of such films has become possible with modern surface science methods, but even if a large variety of experimental data exists, precise atomistic structural models remain difficult to construct. With their predictive power, first-principles calculations are obviously an ideal supplement to the experimental techniques, but their application to such complex systems is still in their infancy.

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In the work presented here the materials under study are thin films of vanadium oxide on Pd(1 1 1). The growth of vanadium oxides on metal surfaces is currently an active field driven by the need to prepare well characterised vanadium oxide films of varying stoichiometry. The properties of such films can then be studied with surface sensitive techniques that would usually be only applicable to metallic surfaces. For our first-principles study we have chosen Pd as support, since a considerable amount of data has accumulated in recent years for thin films of vanadium oxides grown on Pd(1 1 1), including core-level spectra [5], scanning tunnelling microscopy (STM) images [5–7], high resolution electron energy loss spectroscopy (HR-EELS) [8], and near-edge X-ray absorption fine structure (NEXAFS) data [5]. Despite the wealth of information, it turned out to be difficult to derive atomistic models for most of the observed phases. Part of the problems are related to the fact that vanadium can occur in various oxidation states ranging from $V^{2+}$ (VO) to $V^{5+}$ ($V_2O_5$), and unfortunately the stoichiometry is difficult to determine from V core-level spectra alone, since the core levels are significantly affected by the metallic substrate. On the other hand, the experimental data allow to narrow the structures one has to investigate in first-principles calculations. For instance, (2 × 2) STM images and LEED patterns were observed under a variety of experimental conditions. Even though the stoichiometry could not be determined by experiments alone, it was fairly straightforward to construct a number of plausible atomistic models, to test their local stability with first-principles methods, and to compare experimental and theoretical vibrational frequencies and STM images. In our recent work, we established in this way that the available experimental data for the (2 × 2) superstructure can be reconciled with a novel s-$V_2O_3$ phase which has no equivalent in the bulk [6].

Here, our aims are somewhat more ambitious: we want to determine the stable structures for varying stoichiometries and coverage by means of the energies predicted by first-principles calculations. To construct the required phase stability diagram, we need to explore a large number of stoichiometries and reconstructions. Of course such calculations necessarily face limitations, since the investigations must be restricted to a selected number of superstructures. Here, we have limited our calculations to $(\sqrt{3} \times \sqrt{3})$ and (2 × 2) supercells, where reconstructions with a periodicity of (1 × 1) and (2 × 1) are also implicitly covered. Significantly larger systems are difficult to treat, since also a large number of models must be considered at a specific stoichiometry and periodicity. On the other hand, the experiments seem to justify our choice, because with one exception no long range ordered superstructure was observed experimentally. The exception is a VO$_2$ phase [7], which seems to be incommensurable with the Pd(1 1 1) substrate, also implying that the phase cannot be studied in a straightforward manner in a super cell calculation. To assert the stability of such incommensurable phases we will also present results on thin unsupported vanadium oxide films.

Even with the restriction to $(\sqrt{3} \times \sqrt{3})$ and (2 × 2) superstructures, the number of explored models remains large. In some cases, symmetry arguments and/or chemical intuition can help to restrict the choices further, but intuition is often prone to failure. To be less biased simulated annealing runs were often performed to establish that the investigated structures are indeed global energy minima. In total, more than 50 models were constructed and tested in the course of this work, but we will necessarily restrict the discussion mainly to more favourable configurations. We will show that three very different categories of oxides are stable on the surface. The first category is similar to bulk like $V_2O_5$ (corundum), with an oxygen termination at the vacuum and an oxygen layer at the interface. The second class of oxides are thin rectangular or hexagonal vanadium-dioxide films, which interact only weakly with the substrate. Finally, one surface stabilised phase exits (s-$V_2O_3$), which was already investigated in some detail in Ref. [6].

The paper is organised in the following way. We will first briefly discuss the methods used in the present work (Section 2). Then results for bulk vanadium oxides (Section 3.1) and for unsupported oxide films are presented (Section 3.2). The insight gained from these calculations is used to construct models for thin supported oxide films (Sections 3.4–3.7), and the general principles which
govern the stability of thin vanadium oxide films on Pd(111) are discussed in Section 4.2. In Section 4.1 our results are confronted with the experimental data.

2. Methodology

2.1. First-principles calculation

Our first-principles calculations are based on density-functional theory (see eg. Refs. [9,10]) and employ a plane wave basis set [11,12]. As in our previous work (see Ref. [6]) we use the Vienna ab-initio simulation package (VASP) [13–15], where in the most recent version the interaction between the ions and electrons is described by the projector augmented wave (PAW) [16] method in the implementation of Kresse and Joubert [17]. The technical parameters are identical to Ref. [6]: the Pd surface is modelled by a four layer Pd slab (two layers are allowed to relax), and the lattice constant is fixed to the theoretical Pd fcc lattice constant (a_{theory} = 3.95 Å, a_{exp} = 3.89 Å). The generalised gradient approximations (GGA) of Perdew and Wang [18,19], commonly referred to as PW91, are used throughout this work.

To sample the band-structure a grid corresponding to 8 × 8 × 1 k-points in the primitive surface cell is chosen. For a (2 × 2) supercell this corresponds to 4 × 4 × 1 k-points. We did careful tests to ensure that the results are well converged with respect to the slab thickness and with respect to the k-point sampling. When we increased the slab thickness from four to six layers and increased the k-point grid to 6 × 6 × 1 points for the (2 × 2) s-V2O5 model (see Ref. [6]), the adsorption energies changed by less than 15 meV. Hence, we expect that the average errors in the reported energies are about 20 meV, which is sufficient for the present purpose.

2.2. Energy stability of explored models

To characterise the stability of the explored models, we use a generalised adsorption energy \(E_{\text{ad}}\) defined as

\[
E_{\text{ad}} = E_{V,\text{O},/\text{slab}} - (E_{\text{slab}} + N_{\text{Pd}} \mu_{\text{Pd}}) - N_{V} \mu_{V} - N_{O} \mu_{O}.
\]  

(1)

\(E_{V,\text{O},/\text{slab}}\) and \(E_{\text{slab}}\) are the energies of the explored model and the clean Pd-slab, respectively. The models allow for a replacement of surface or subsurface Pd atoms by V atoms, or the addition of Pd atoms to the surface, and the number of Pd atoms removed or added to the slab is denoted by \(N_{\text{Pd}}\). We must allow for such processes, since Pd atoms are available on the surface by evaporation from steps. In equilibrium, the chemical potential of a Pd atom is given by \(\mu_{\text{Pd}} = E_{\text{Pd}}(\text{fcc})\), since – in simple terms – the average energy for removal of a step atom equals the energy of an atom in the bulk. With respect to Pd, the grand-canonical potential is effectively considered assuming equilibrium between the surface and the bulk. The reference energy for V, \(\mu_{V}\), is set to the energy of a bcc bulk V atom, and \(\mu_{O}\) is set to half of the energy of an oxygen dimer. These two values define the energy zero for O and V, but we will discuss below that results do not depend on the precise reference values.

To establish the stability of a particular structure we first calculate the average energy of formation per ad-atom

\[
E_{\text{form}} = \frac{E_{\text{ad}}}{N_{V} + N_{O}},
\]  

(2)

and plot this value against the concentration of V atoms

\[
x_{V} = \frac{N_{V}}{N_{V} + N_{O}}.
\]  

(3)

As will be shown at the end of this paragraph, this quantity can be used to assess the stability of a particular structure as long as part of the Pd surface is not covered by any adsorbate (free surface area is accessible). In this case, stable structures are those which lie on a concave curve, as illustrated in Fig. 1. This is similar to the construction of the phase diagram of a binary alloy, and to show that this description is correct, we resort to the usual arguments based on the surface energy. The most stable structure will result in the lowest surface energy, and it is easy to see that adsorption
of an oxide in the structures A, B and C decreases the total surface energy by $\Delta E_{\text{surf}}^x = N_x E_{\text{form}}^x$, where $N_x$ is the total number of adsorbed atoms. Exactly the same quantity, $N_x E_{\text{form}}^x$, determines the stability of binary alloys, which immediately shows the validity of the previous argument. The second important point is that a redefinition of the reference energies of oxygen, $\mu_O$, or vanadium, $\mu_V$, will redefine only the slopes of all lines, but the stability considerations will not be affected. We stress again, that this approach works only in the low coverage limit, since it assumes that phases can freely decompose into other phases consuming free surface area.

To discuss the case when the whole Pd surface is covered with an oxide, we have to use an alternate description. We define the change in the surface energy per surface area as

$$\Delta E_{\text{surf}} = \frac{E_{\text{ad}}}{n_{\text{cell}}}, \quad (4)$$

where $n_{\text{cell}}$, is the number of primitive surface cells in the slab model. Similar to the previous case the chemical potential of Pd is set to $\mu_{\text{Pd}} = E_{\text{Pd}}(\text{fcc})$, which simply assumes that the surface is in equilibrium with bulk Pd. The chemical potential of vanadium, $\mu_V$, is again set to $E_V(\text{bcc})$, but the final results will not depend on this choice. The chemical potential of oxygen, $\mu_O$, is now treated as an extrinsic thermodynamic variable, which is supposed to be determined by the experimental setup. Then we plot the change in the generalised surface energy, $\Delta E_{\text{surf}}$, for each structure versus the nominal V coverage of this structure for a set of $\mu_O$ (for more details see Section 4.1). Along similar arguments as before, it can be shown that stable phases must lie again on a concave curve (compare again Fig. 1), but now the oxygen potential is an extensive (externally controlled) degree of freedom. On the other hand, a redefinition of the chemical potential of V will again only change the slope of all lines by the same value, so that the stability considerations are not affected by such a change. The approach taken here is similar in spirit to the stability considerations of surfaces of compounds [20–23] but complicated by the fact that we have to consider three constituents instead of two. In addition, we transform to the grand-canonical potential only with respect to oxygen and treat the V coverage as the second extensive thermodynamic variable. This description was chosen, since it corresponds to the experimental setup in which the V coverage and the oxygen partial pressure are controlled [5,6].

3. Results

3.1. $V_xO_y$ bulk phases and convergence tests

To check the accuracy of the setup, first-principles calculations for four bulk vanadium oxide phases and oxygen chemisorbed on Pd(111) were performed, paying particular attention to the oxygen potential and the energy cutoff. Further results, in particular results for low symmetry and low temperature $V_xO_y$ phases and a discussion of electronic properties will be published elsewhere, since this is beyond the scope of the present work [24].

Table 1 summarises the lattice constants of the considered oxides and compares them with experimental data. The heat of formation with respect to bulk V and the $O_2$ dimer are shown in Fig. 2. All bulk calculations and the surface calculations reported in the later sections were performed with a rather “soft” oxygen potential at an
Table 1
Lattice constants of bulk vanadium and vanadium oxides considered in the present work. Also shown is the bond length of the oxygen dimer (all values in Å).

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Type</th>
<th>Experiment</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>Dimer</td>
<td>a = 1.21</td>
<td>a = 1.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a = 11.51,</td>
<td>b = 11.65,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b = 3.57,</td>
<td>b = 3.57,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 4.37&lt;sup&gt;a&lt;/sup&gt;</td>
<td>c = 4.69</td>
</tr>
<tr>
<td>VO₂</td>
<td>Rutile</td>
<td>a = 4.55</td>
<td>a = 4.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 2.85&lt;sup&gt;b&lt;/sup&gt;</td>
<td>c = 2.80</td>
</tr>
<tr>
<td>V₂O₃</td>
<td>Corund. RAF</td>
<td>a = 4.94</td>
<td>a = 4.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 13.97&lt;sup&gt;c&lt;/sup&gt;</td>
<td>c = 14.25</td>
</tr>
<tr>
<td>VO</td>
<td>NaCl</td>
<td>a = 4.07&lt;sup&gt;d&lt;/sup&gt;</td>
<td>a = 4.19</td>
</tr>
<tr>
<td>V</td>
<td>bcc</td>
<td>a = 3.03</td>
<td>a = 2.99</td>
</tr>
</tbody>
</table>

RAF refers to the anti-ferromagnetic ordering described in Ref. [33].
<sup>a</sup>Ref. [25].
<sup>b</sup>Ref. [28].
<sup>c</sup>Ref. [29].
<sup>d</sup>Ref. [34].

The oxygen richest compound is V₂O₅, which forms a layered structure and is an insulator. Our final structural data agree well with the experimental data [25] and to a lesser extent with previous theoretical calculations (in Refs. [26,27], the local density approximation was used leading to an underestimation of all lattice parameters). Only the distance between the V₂O₅ layers is significantly overestimated, which we attribute to the fact that gradient corrected functionals do not account very accurately for Van der Waals bonding.

VO₂ [28] and V₂O₃ [29] were considered only in the metallic high temperature phases (rutile and corundum structure respectively) and we find for both structures reasonable agreement with experiment. The low temperature phases are Mott-Hubbard insulators [30], for which present density functionals fail to work satisfactory [31–33].

Bulk VO [34] was initially investigated in the NaCl structure, for which the lattice constant is significantly overestimated compared to experiment. In addition, Fig. 2 shows that VO decomposes into V and V₂O₃. If 25% vanadium and 25% oxygen vacancies are introduced by removing one V atom and one O atom from the edge of the VO<sub>2</sub> cube, VO becomes stable (a similar vacancy structure was reported for NbO) [35]. In this case, the lattice constant is smaller than in the experiment, which could be attributed to disorder or to a reduced vacancy concentration in real VO.

As an additional test, the adsorption energy of atomic oxygen on Pd(1 1 1) in the p(2 × 2) structure was calculated. We found a value of 1.36 eV with respect to half an O₂ dimer. Careful tests for oxygen adsorption on Pd(1 1 1) and for several vanadium oxide structures with a harder and more accurate oxygen potential at an energy cutoffs of 500 eV indicate that all calculated energies are accurate to within 20 meV, which we consider to be sufficient for the present purpose.

In passing, we want to point out that for an oxidation state between +III and +V, vanadium atoms typically prefer an octahedral environment. VO, corundum V₂O₃, rutile VO₂ and even V₂O₅.

![Fig. 2. Formation energy of bulk and film vanadium oxides.](image-url)

Filled triangles correspond to bulk phases, circles to thin film phases (see text). The two circles at the stoichiometry VO₂ correspond to the hexagonal (upper circle) and the rectangular (lower circle) VO₂ film.
can be build by a proper arrangement of such octahedrons. The V–O bond-length increases from 1.91 Å in VO₂, over 1.97 Å in V₂O₅ to 2.09 Å in VO. One can expect that such building units will remain relevant in thin films and thin films grown on the Pd(1 1 1) surface.

3.2. Thin unsupported layers

Before considering vanadium oxides grown on Pd(1 1 1), we will briefly discuss the stability of few thin unsupported oxide layers. These calculations are partly motivated by the fact that an incomensurable oxide layer was observed to grow on Pd(1 1 1) under certain experimental conditions (VO₂ phase, see Refs. [5, 7]). Since the interaction of such a layer with the substrate is weak, it seems reasonable to model such a layer without the Pd support. Secondly, results for thin unsupported layers are helpful for the construction of compact oxide layers which are commensurable with the Pd(1 1 1) surface, and many of the oxides considered in later sections resemble the thin films discussed below.

One way to construct such thin layers is by cleaving vanadium oxides along low index symmetry planes. If one follows this route for oxygen rich oxides – like VO₂ or V₂O₃ – and cleaves in a way that leaves the stoichiometry conserved, the octahedral environment of V atoms is strongly disturbed, and such models are generally not particularly favourable. If, on the other hand, all O–V bonds around V atoms are left intact, unreasonable V oxidation numbers are often obtained also leading to instabilities. This problem can be surmounted by cleaving e.g. VO so that the octahedral environment around V atoms is left intact.

We start with the highest oxidation number of vanadium corresponding to V₂O₅. Since V₂O₅ is a layered structure and since the interaction between the layers is known to be weak [26, 27], a single V₂O₅ layer is very stable. We found a formation energy of $E_{\text{form}} = -2.30$, which is only some 10 meV less than for bulk-V₂O₅.

For V₄O₉, bulk-V₂O₅ was cleaved parallel to two basal planes, leaving three O₃ and two V₂ planes with a stacking sequence of O₁V₂O₃V₂O₃. Thinner layers are unfavourable, since the oxidation number of V becomes either unreasonable or the vanadium coordination is disturbed significantly, as discussed before. The formation energy of the V₄O₉ model is $-2.22$ eV, and the substrate supported case of this structure is shown in Fig. 3(c). The structure shows only negligible spin polarisation in contrast to the bulk-V₂O₃ phase.

![Fig. 3. Structures discussed in this work. Supercells with $(\sqrt{3} \times \sqrt{3})$ periodicity: (a) one layer of bulk-like V₂O₃ on Pd(1 1 1) with the vacuum side only oxygen terminated, (b) bulk-like V₂O₅ with both sides oxygen terminated, (c) two layers of bulk-like V₂O₃ on Pd(1 1 1) both sides oxygen terminated. Supercells with with $(2 \times 2)$ periodicity: (d) s-V₂O₃ and (e) hexagonal VO₂ with s-V₂O₃ on top. For structure (e) the V atoms in the topmost layer have either an octahedral (dashed) or a tetrahedral (dotted) coordination. The average distance between the layers is indicated on the right (all distances in Å).](image-url)
At the stoichiometry VO$_2$, three models were considered, all obtained by cleaving bulk VO. In the first case, VO was cleaved along two (111) planes leading to a hexagonal layer of V atoms and two also hexagonal oxygen layers above and below the V atoms (see Fig. 4(a)). Initially, the lattice constant of such a model is \( a = 3.62 \) Å, but structural relaxation to the groundstate leads to a reduction of the lattice constant to \( a = 2.87 \) Å, which is close to that of the Pd(111) surface. The height of the model is 2.04 Å (oxygen core-core distance). The formation energy is \( E_{\text{form}} = -2.25 \) eV, and each V atom has a magnetic moment of 1\( \mu_B \).

Cleavage along the (110) plane of VO is somewhat more complicated, since in the (110) direction a plane contains the same number of vanadium and oxygen atoms. We keep two adjacent vanadium oxide planes and add from two additional planes the oxygen atoms only, so that the octahedral coordination of vanadium atoms is maintained. The final structure is visualised in Fig. 4(b). The initial lattice constants are \( a = 2.88 \) Å and \( b = 4.07 \) Å and relax to \( a = 2.96 \) Å and \( b = 3.71 \) Å. The height of the model is 4.2 Å. With a formation energy of \( -2.34 \) eV, this structure is more stable than the previous hexagonal model, and, as will be discussed in Section 4.1, the lattice parameters agree well with the thin VO$_2$ phase of Ref. [7]. In the rest of this work, we will refer to this model as rectangular VO$_2$ film. The magnetic moment of each vanadium atom is again 1\( \mu_B \).

Finally, cleavage along the (100) plane of VO was considered. Again two adjacent vanadium oxide planes were kept, and the oxygen atoms of two additional layers added on the top and bottom in a way that leaves the local coordination of V atoms intact. It turns out that this is the most unfavourable cleavage plane for VO, and the formation energy is only \( -2.08 \) eV.

Further reduced oxide layers were not considered, since the octahedral coordination of V atoms would be significantly disturbed in these cases. Generally such models are found to be rather unfavourable. The energies of the thin films discussed until now are compared to the formation energies of bulk phases in Fig. 2.

3.3. Simulated annealing run for a (4 × 4) stepped surface

To gain insight which structures are preferred by vanadium oxides on the Pd surface in the low coverage case, we performed a short finite temperature molecular dynamics (MD) simulation. The Pd surface was modelled by a stepped (4 × 4) supercell. Only three layers were included in the
calculation, and the bottom layer was kept fixed during the MD simulation. Six vanadium and four oxygen atoms were placed on the surface, all initially occupying hollow sites. The temperature during the simulation was set to 1200 K and gradually decreased to 300 K. Since the total simulation time was relatively short (4 ps), we cannot expect to find the real zero temperature equilibrium groundstate but hope to get some indication for the preferred positions of V and O atoms.

The final structure for the $V_2O_4$/Pd MD simulation is shown in Fig. 5. One V atom has replaced a surface Pd atom which has in turn diffused to the step (arrows in Fig. 5). A second V atom occupies a three fold hollow site, and the remaining four V atoms have attached to the step. Three of the oxygen atoms are bridge bonded between two V atoms. The remaining fourth oxygen atom is coordinated to the V atom in the hollow site.

The results can be rationalised in the following way. First, a strong tendency towards V–Pd hetero-coordination exists. This is also confirmed in first-principles calculations for the adsorption of V on Pd (see Ref. [36]). Here we want to summarise only the most important results of these calculations. In the V–Pd surface alloy, V atoms try to maximise their coordination to Pd atoms. V atoms on the surface prefer the hollow sites but are unstable towards diffusion into the surface or bulk. If a V atom replaces a surface atom, it gains an energy of $E_{\text{form}} = -0.8$ eV, and V atoms in subsurface sites or the formation of a dilute V–Pd bulk alloy yields an energy gain of the order of $E_{\text{form}} = -1.8$ eV per V atom. The MD simulation presented here shows that the trend towards V–Pd hetero-coordination prevails in the case of oxidised V atoms: V atoms prefer positions in which the coordination to Pd atoms is large (substitutional surface sites, step edges and hollow sites). Our MD also clearly shows that the oxygen atoms tend to bind to V atoms and not to surface Pd atoms. This is an indication for the strong reactivity of V.

In addition, the oxygen atoms are preferentially bonded to more than one V atom, and the bridge bonded position between two V atoms is particularly favourable.

3.4. General strategies for the construction of surface models

With the calculations presented so far we are armed with the required insight to build more complex models for vanadium oxides on Pd(1 1 1). For “compact” layers, i.e. a V-coverage exceeding about 1/2 ML, one can expect similar structures as for bulk or thin unsupported vanadium oxide layers, whereas for small V concentrations the results of the MD should prove useful: V atoms prefer sites in which the Pd coordination is maximised, and oxygen atoms are preferentially bridge bonded. In the construction of starting models, we have therefore adopted three different strategies: (i) For compact over-layers, the starting models are similar to the thin film phases discussed in Section 3.2. Only two structures are commensurate with the hexagonal Pd(1 1 1) surface. These are bulk-$V_2O_3$ (and the corresponding thin films) and the hexagonal thin VO$_2$ film. Even with this restriction, a large number of different stacking sequences has to be explored. (ii) For small vanadium coverage one must proceed along a different line. It turns out that the most successful strategy is to place vanadium atoms at their preferred sites (Pd-surface sites, hcp and fcc hollow sites) and to
add oxygen atoms in a way that they are bonded to at least two V atoms. Since the oxygen–vanadium bond length is typically around 1.8 Å, sensible distances between two vanadium atoms range from 2.8 to 3.6 Å. This leaves only very few useful configurations: for instance, two vanadium atoms in two neighbouring fcc (hcp) hollow sites, or one V in a hcp and the second one in the second nearest fcc site. If V atoms occupy surface sites, oxygen can only coordinate to two V atoms, if the V atoms occupy neighbouring surface sites. (iii) Finally, in some cases, simulated annealing runs were used either to get new structural models or to confirm the global stability of one particular model.

The energies of the most relevant phases are summarised in Table 2, and the energies of the important low coverage phases are shown in Fig. 6. On the left-hand side of the energy diagram (oxygen rich case), the most stable phase is the oxygen p(2 × 2) phase, where oxygen atoms are adsorbed in fcc hollow sites at 1/4 ML. With respect to an oxygen dimer, the energy gain upon adsorption is 1.36 eV per oxygen atom.

On the right-hand side of the diagram (no oxygen), the largest energy amount can be gained by diffusion of V atoms into the Pd bulk. In this case, each V atom gains 1.81 eV [36]. For the migration of V into the bulk, barriers must be overcome and depending on the experimental preparation this configuration might not be always accessible [36]. If the diffusion of V to the bulk is in some

![Fig. 6. Formation energy $E_{\text{form}}$ versus composition $x$ for vanadium oxides on Pd(111) (structural models are discussed in the text). For comparison, the bulk formation energies of $V_2O_3$, $VO_2$, $V_2O_3$ and VO are shown as filled triangles. Table 2 summarises the relevant phases.

<table>
<thead>
<tr>
<th>Shortcut</th>
<th>V-coverage (ML)</th>
<th>$E_{\text{form}}$ (eV)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>p(2 × 2)-O</td>
<td>0</td>
<td>-1.360</td>
<td>O adsorbed in the p(2 × 2) structure</td>
</tr>
<tr>
<td>$V_2O_3$</td>
<td>0.659</td>
<td>-2.300</td>
<td>Single layer of bulk-$V_2O_3$</td>
</tr>
<tr>
<td>$V_2O_5$</td>
<td>2/3</td>
<td>-2.281</td>
<td>One layer of bulk-$V_2O_5$, vacuum side O-terminated (Fig. 3(a))</td>
</tr>
<tr>
<td>$V_4O_8$</td>
<td>4/3</td>
<td>-2.184</td>
<td>Two layers of bulk-$V_2O_3$, vacuum side O-terminated</td>
</tr>
<tr>
<td>$V_8O_{12}$</td>
<td>6/3</td>
<td>-2.232</td>
<td>Three layers of bulk-$V_2O_3$, vacuum side O-terminated</td>
</tr>
<tr>
<td>$V_2O_6$</td>
<td>2/3</td>
<td>-1.992</td>
<td>One layer of bulk-$V_2O_3$, both sides O-terminated (Fig. 3(b))</td>
</tr>
<tr>
<td>$V_4O_8$</td>
<td>4/3</td>
<td>-2.316</td>
<td>Two layers of bulk-$V_2O_3$, both sides O-terminated (Fig. 3(c))</td>
</tr>
<tr>
<td>$V_8O_{12}$</td>
<td>6/3</td>
<td>-2.334</td>
<td>Three layers of bulk-$V_2O_3$, both sides O-terminated</td>
</tr>
<tr>
<td>$s-V_2O_3$</td>
<td>1.23</td>
<td>-2.376</td>
<td>Thin rectangular layer (see Fig. 4(b))</td>
</tr>
<tr>
<td>$h-V_2O_3$</td>
<td>1</td>
<td>-2.335</td>
<td>Thin hexagonal layer (see Fig. 4(a))</td>
</tr>
<tr>
<td>$s-V_2O_3$</td>
<td>1/2</td>
<td>-2.540</td>
<td>$s-V_2O_3$ (Fig. 3(d))</td>
</tr>
<tr>
<td>$V_2O_5$</td>
<td>1.5</td>
<td>-2.376</td>
<td>(2 × 2) h-$VO_2$ plus an overlay of $s-V_2O_3$ (see Fig. 3(c))</td>
</tr>
<tr>
<td>$V_4O_{12,3}$</td>
<td>1</td>
<td>A monolayer of V, with O adsorbed in hollow sites</td>
<td></td>
</tr>
<tr>
<td>$V_6O_{12,2}$</td>
<td>3/4</td>
<td>Three V atoms replacing Pd surf.-atoms, O adsorbed in hollow sites</td>
<td></td>
</tr>
<tr>
<td>$V_{\text{ad}}$</td>
<td>Any</td>
<td>-1.8</td>
<td>V forming a solid solution in fcc Pd</td>
</tr>
</tbody>
</table>
way hindered, another plausible configuration is a surface alloy with a stoichiometry of Pd\textsubscript{1}V. The most stable bulk structure at this stoichiometry is the Al\textsubscript{1}Ti structure with a formation energy of $-0.915$ eV per V-atom. Similar values are found for simple surface alloys in which every fourth Pd surface atom is replaced by a V atom [36].

In the following sections, we will discuss the results at different stoichiometries in more detail. The discussion will first focus on the bulk-V\textsubscript{2}O\textsubscript{3} derived structures and the V\textsubscript{2}O\textsubscript{3} stoichiometry, since particularly stable configurations can be observed in these cases. Then we will focus on the oxygen rich regime and finally on the (less interesting) vanadium rich regime. A description of the investigated phases is summarised in Table 2.

### 3.5. Phases derived from bulk-V\textsubscript{2}O\textsubscript{3}

Experiments show that bulk-like V\textsubscript{2}O\textsubscript{3} grows epitaxially on the Pd(1 1 1) surface. A consideration of the lattice constants of V\textsubscript{2}O\textsubscript{3} (experiment $a = 4.91$ Å, theory $a = 4.90$ Å) shows that this fits well with the lattice constant of the $(\sqrt{3} \times \sqrt{3})$ Pd(1 1 1) surface (experiment $a = 4.764$ Å, theory $a = 4.842$ Å) supporting the experimental findings. To study this case, one, two and three layers of bulk-V\textsubscript{2}O\textsubscript{3} on Pd(1 1 1) were explored. We considered stackings with oxygen and vanadium at the interface and different terminations at the vacuum side. In general, our calculations clearly indicate that oxygen is located at the metal–oxide interface and the vacuum side at the relevant chemical potentials of oxygen. For thin layers, this causes an increase in the oxygen content $V_{2}O_{3+x}$ compared to bulk-V$_{2}$O$_{3}$.

Let us, nevertheless, start with one and two layers of stoichiometric bulk-V$_{2}$O$_{3}$. The most favourable stacking sequences are Pd–V$_{2}$–O$_{3}$ (one layer) and Pd–V$_{2}$–O$_{3}$–V$_{2}$–O$_{3}$ (two layers), where the V atoms are located in the hcp sites and O atoms are situated atop Pd sites (see Fig. 3(a)). For a single layer of vanadium oxide the formation energy is $E_{\text{form}} = -2.28$ eV and it decreases to $E_{\text{form}} = -2.18$ eV for the double layer. Both values are smaller than the bulk values ($E_{\text{form}} = -2.32$ eV), which we attribute to finite size effects (formation of the surface and the interface). When additional layers are added the energy gain per added layer equals that of bulk-V$_{2}$O$_{3}$, so that the formation energy of thicker layers converges towards the bulk-V$_{2}$O$_{3}$ value (e.g. V$_{6}$O$_{9}$, see Table 2).

For the cases, in which oxygen is located at the interface and the vacuum side, we started our calculations with a single layer corresponding to O$_{1}$V$_{2}$O$_{3}$. Formally this corresponds to a stoichiometry of VO$_{3}$, which can and does not exist in a bulk-like phase (a thin film of this type is unstable too). But here one oxygen layer is in contact with the Pd surface leading to a covalent bonding between the oxide and the Pd surface (if the film is brought from the vacuum to the Pd-surface, 3.5 eV are gained per V$_{2}$O$_{6}$ unit). The most favourable stacking sequence is Pd(A)–Pd(B)–Pd(C)–O(A)–V(B)–O(C) (see Fig. 3(b)), where A, B and C are used to label the layers in the fcc crystal. The Pd–O distance is 2.1 Å, which is only slightly larger than the distance between atomic oxygen and Pd, corroborating the existence of a covalent bond between the oxygen layer and the Pd substrate. Among the explored stacking sequences was also one recently proposed by Jennison et al. for O$_{1}$Al$_{2}$O$_{3}$ on fcc-Al, in which Al and V, respectively, have a tetragonal coordination (stacking: Pd(A)–Pd(B)–Pd(C)–O(A)–V(A)–O(C)) [37]. We found this model to be less favourable in the present case (100 meV/atom), which relates to the fact that the tetragonal coordination is not favoured by V in any oxidation state.

The stability is much enhanced for two layers bulk-V$_{2}$O$_{3}$ (O$_{1}$V$_{2}$O$_{3}$V$_{2}$O$_{3}$), corresponding to a stoichiometry of V$_{4}$O$_{9}$ (compare Fig. 3(c)). As a result of the reduced oxygen concentration, the bonding to the substrate is much weaker and the distance of the ad-layer is larger than for a single layer. The weaker substrate binding is also reflected by the energy gain for bringing the oxide from the vacuum to the surface which is now only 1.3 eV (440 meV for each O–Pd bond). Also the most stable stacking sequence is different, and the oxygen atoms are now situated above the Pd sites (the typical Pd–O bond length is again some 2.1 Å). The results for three layers can be found in Table 2 (V$_{6}$O$_{12}$).
3.6. Surface stabilised phases

With the restriction to \((2 \times 2)\) and \((\sqrt{3} \times \sqrt{3})\) models, we have to consider only one additional case for the stoichiometry \(V_2O_3\); \(V_2O_3\) in a \((2 \times 2)\) supercell. The most stable structural model is shown in Fig. 3(d). The V atoms now adsorb in a honeycomb pattern (fcc and hcp sites) and O binds to the V–V bridge sites. For this structure the formation-energy \(E_{\text{form}} = -2.54 \text{ eV}\) is larger than for bulk-like \(V_2O_3\), and we will refer to the model in the following as \(s-V_2O_3\) (surface-\(V_2O_3\)). For \(s-V_2O_3\) and a single bulk-like \(V_2O_3\) layer, the O–V bond length at the vacuum side is 1.77 Å. For \(s-V_2O_3\), the oxygen atoms are located exactly at V–V bridge sites, whereas they are moved off bridge for bulk-like \(V_2O_3\), forming an almost ideal hexagonal layer (Fig. 3(a)). The reason for the increased stability of \(s-V_2O_3\) compared to bulk-\(V_2O_3\), is most likely electrostatics. Since the packing of oxygen atoms is significantly lower for this model (2/3 compared to 1 ML for bulk-like \(V_2O_3\)), the mutual repulsion between \(O^{2-}\) ions is decreased. It is important to stress that \(s-V_2O_3\) is only stable in this thin-film configuration and even the addition of a second layer is energetically very unfavourable [7].

Before continuing, we mention here that we recently identified the \(s-V_2O_3\) structure to be responsible for the experimentally observed \((2 \times 2)\) LEED pattern and STM images [6]. This identification was also supported by simulated core-level shifts and the comparison of the vibrational frequency of the dipole active mode with HR-EELS.

3.7. Thin film phases

The hexagonal \(VO_2\) thin-film phase (compare Fig. 4(a)) is almost commensurate with the substrate, hence we modelled the pseudo-morphic growth of the layer on Pd. On the surface, we found a formation energy of \(-2.33 \text{ eV}\), which corresponds to a binding energy of 410 meV per Pd–O bond (compared to the isolated h-\(VO_2\) film). A very similar value was already found for the interface energy of the bulk-\(V_2O_3\) \(_{3+x}\) phases in Section 3.5. The local coordination of the oxygen atoms is also similar (O above Pd sites). We have also tried to add an add-layer of \(s-V_2O_3\) on top of this hexagonal thin film, corresponding to \(4(h-VO_2)/s-V_2O_3\) (\(V_2O_{11}\)). As will be seen later, this is a very stable phase at higher V coverage. The stable stacking sequence is shown in Fig. 3(e), where, interestingly, half of the vanadium atoms have a tetrahedral coordination in the topmost layer. Stacking sequences without tetrahedrally coordinated V atoms would require that the topmost oxygen layer were located exactly above the central oxygen layer, which is electrostatically unfavourable.

The rectangular \(VO_2\) model (compare Fig. 4(b)) cannot be modelled with the support. But if we assume a smoothly varying Pd–O energy surface which resembles that for the hexagonal over-layer (410 meV atop, 140 meV in the bridge and 100 meV above hollow), and if we further assume that the oxygen atoms at the substrate–oxide interface are randomly distributed, we obtain a typical substrate–oxide binding energy of

\[
1/4 \cdot 400 \text{ meV} + 2/4 \cdot 140 \text{ meV} + 1/4 \cdot 100 \text{ meV} \\
\approx 200 \text{ meV}
\]

per oxygen atom in contact with the surface. The average formation energy is then \(-2.38 \text{ eV}\), more stable than the h-\(VO_2\) film.

At this point, it is also instructive to consider the two bulk phases corresponding to the stoichiometries under consideration. \(V_2O_3\) and thin layers of \(V_2O_5\) are more stable than any of the surface oxides considered here (see Fig. 6). From a thermodynamic point of view, we would expect that \(V_2O_3\) grows on Pd (see also Section 4.1). The growth of such a layer is however likely to be kinetically hindered by the strong corrugation of \(V_2O_3\). Bulk-\(VO_2\) is also fairly stable, and its energy is slightly lower than that of the rectangular phase. But as already discussed in Section 3.2 thin films of bulk-\(VO_2\) are generally not favourable, which makes the formation of a nucleus of \(VO_2\) on Pd(1 1 1) also unlikely.

3.8. VO stoichiometry, and further reduced oxides

In our study, a significant effort was devoted to the investigation of the 1:1 stoichiometry, since initially it was assumed that the experimentally observed \((2 \times 2)\) superstructure corresponds to
this stoichiometry. More than 10 models in a 
(2 × 2) supercell were explored at this particular 
composition, and the number of V and O atoms 
varied between one and four atoms per (2 × 2) 
supercell. The general result of our investigation, 
however, is that none of these structures are ther-
modynamically stable. Even the most stable ones 
will decompose into V forming a solid solution in 
Pd and s-V$_2$O$_3$, with an energy gain of about 200 
meV per surface atom.

At the lowest considered coverage (1/4 and 1/2) 
the V atoms replace surface Pd atoms, and the 
oxide atoms adsorb in a way which maximises 
their coordination to the V atoms. At 1 ML V and 
O coverage, the oxide forms a compact overlayer, 
with the most favourable stacking sequence being 
Pd(A)–Pd(B)–Pd(C)–V(B)–O(C). The local coor-
dination of the V atoms at the interface is simi-
lar to that for bulk-V$_2$O$_3$, grown on Pd(1 1 1) and 
s-V$_2$O$_3$ (see Section 3.5). The results for the VO 
stoichiometry clearly confirm the trend towards 
V–Pd hetero-coordination already observed in the 
simulated annealing run, insofar, that at low oxida-
tion numbers, the V atoms try to maximise their 
coordination to Pd atoms, preferentially, by re-
placing surface Pd atoms.

It is also important to stress that bulk VO is 
even less stable than the surface structures ex-
plored here so that the formation of a thick bulk 
VO phase on the Pd substrate is not possible. The 
calculated energies clearly show that, in the vicin-
ity of a Pd surface, bulk VO will always decompose 
into V$_2$O$_3$ and V atoms forming a solid solution 
in Pd.

From these calculations, it is obvious that a 
 Further reduction of the vanadium oxide layer 
will always be accompanied by a tendency towards 
V–Pd hetero-coordination. The most stable model 
which we could determined for such films is 
characterised by three V atoms replacing Pd sur-
face atoms and two oxygen atoms situated in those 
hollow sites which are surrounded by three V 
atoms (for details we refer to Ref. [6]). To explore 
 further reduction we have considered adsorption of 
oxide on a Pd-supported close-packed mono-
layer of V (models V$_4$O$_1$, V$_4$O$_2$ and V$_4$O$_3$), and a 
model in which three Pd surface atoms are re-
placed by V atoms and one O atom is placed in a 
hollow site (V$_3$O$_7$). In general, none of these 
structures are particularly stable, and, in all cases, 
a combination of V$_2$O$_3$ and vanadium in a bulk 
solution or the formation of a Pd–V surface alloy 
allows to lower the energy (see Fig. 6).

4. Discussion

4.1. Comparison with experiment

Comparison with experiment is somewhat 
hampered by the fact, that only limited microscopic 
data (STM) are yet available. To compare with 
experiment, we show the generalised surface energy 
versus the vanadium coverage for two different 
chemical potentials of oxygen, $\mu_O$, in Fig. 7. In 
principle, the chemical potential can be related di-
rectly to the pressure of oxygen, $p_O$, but uncer-
tainties are caused by density functional theory. 
The PW91 gradient approximation has the ten-
dency to overestimate formation and binding 
energies [38,39] which means that the chemical 
potential might be shifted by several 100 meV. A 
change of the potential by 1 eV, corresponds to 
lowering the pressure by a factor of $10^{10}$ at 1000 K, 
and $10^{20}$ at 500 K (at least in the ideal gas regime). 
Using the theoretical binding energy of the oxygen 
molecule as reference, the upper limit for $\mu_O$ is 0, 
corresponding to oxygen molecules condensing 
on the surface (a pressure of course not accessible 
in the experiments). The potentials of $-1.7$ and 
$-2.5$ eV correspond to partial pressures of some 
$10^{-12}$ and $10^{-28}$ bar at $T = 500$ K [40,41], but again, 
the absolute pressures might be wrong by many 
orders of magnitude. We will therefore concentrate 
on the general trend and do not put a strong em-
phasis on the pressure scale.

The diagrams shown in Fig. 7 are easy to read 
(see also Section 2.2). Imagine that we want to 
determine the stability of oxide phases at 1 ML V 
coverage at a given chemical potential, $\mu_O$. In 
the relevant diagram, only the energetically most fa-
vourable phases to the left and right of the 1 ML V 
line are stable. To guide the eye, the most stable 
phases are connected by lines. At $\mu = -1.7$ for 
instance, a mixture of s-V$_2$O$_3$ and r-VO$_2$ is 
expected to exist at 1 ML coverage. The diagram
also indicates that h-VO₂ is unstable under those conditions and decomposes into V₂O₃ and r-VO₂. The top panel indicates the stable phases as a function of the V-coverage and oxygen potential by black lines. At a given coverage and potential, the two phases to the left and right of the considered point are stable (as indicated by the black circle and the arrows in the graph).

At the μ₀ = 0, we find that only bulk-like V₂O₃ phases are thermodynamically stable at any coverage investigated here. The bulk-like V₂O₃ phases are oxygen terminated on both sides (V₂O₆, V₄O₉ and V₆O₁₂) and have no tendency to grow to thicker islands at low coverage and high oxygen pressures. Lowering the chemical potential of oxygen will make structures with high oxygen content less stable. In fact, at a potential of μ₀ = −0.3 eV, the oxygen richest phase, V₂O₆, becomes unstable, and thicker islands start to form even at lower coverage (V₄O₉). At a chemical potential of some μ₀ = −1.3 eV, chemisorbed oxygen on the Pd surface becomes unstable and oxygen evaporates from the Pd surface into the gas phase.

The first phase which is not related to bulk-V₂O₃ becomes stable at a potential of some −1.6 eV at low coverage (s-V₂O₃). At about the same potential (μ = −1.7 eV), the rectangular VO₂ phase is stabilised, and V₄O₉ disappears. At μ₀ = −2.2 eV, the rectangular phase becomes unstable again, and a hexagonal VO₂ phase with s-V₂O₃ on top appears (V₆O₁₁). When we continue to lower the partial pressure further (μ₀ = −2.65 eV), the bulk like V₂O₃ phases (V₆O₁₂) are finally destabilised and vanadium starts to move subsurface. At a similar pressures (μ₀ = −2.5 eV), the hexagonal V₆O₁₁ phase also starts to decompose, and the liberated V atoms go subsurface. Finally at about μ₀ = −3.0 eV, all oxides on the surface decompose, and the vanadium atoms disappear into the bulk.

How do our predictions compare to experiment. First it is clear that the phase diagram predicted by theory is complicated and astonishingly rich. Let us imagine, for instance, that we start from an oxygen rich phase at a nominal vanadium coverage of 1 ML and remove oxygen by slow heating (a similar preparation as used in Refs. [5,6]). At relevant pressures of a few mbar initially only bulk like V₂O₃ islands (V₄O₉) are stable. At μ₀ = −1.6 eV, a phase transition to a mixture of s-V₂O₃ and islands of bulk-V₂O₃ will occur. Decreasing the potential further to μ₀ = −1.7 eV will lead to s-V₂O₃ and patches of rectangular VO₂. Further decrease of the potential will destabilise the rectangular phase in favour of the hexagonal phase with s-V₂O₃ on top. This phase and s-V₂O₃ on Pd are stable over a wide pressure regime. At
μ = −2.6eV, the 4(h-VO2)/s-V2O3 (V6O11) phase decomposes and V diffuses into the bulk, with s-V2O3 wetting the whole Pd surface. With further reduction, finally all V atoms will move subsurface. These results agree very well with experiment, if we relate the rectangular VO2 phase to the VO2 phase observed in Ref. [5] (flower like pattern in LEED) and s-V2O3 to the VO termed phase of Ref. [5]. The last assignment was already shown to be correct in Ref. [6], but the assignment of the rectangular VO2 phase to the “flower-phase” was only confirmed recently by STM and LEED [7].

One final note on bulk-V2O5 is appropriated here. We have included the stability of this phase in all diagrams of Fig. 7 (filled triangles and thin line in the top panel). At low V coverage and for oxygen potentials up to μO = −1.9 eV, V2O5 is energetically stable. This confirms our previous assertions that kinetic instead of thermodynamic arguments must be responsible for the fact that V2O5 was not observed in the experiments. Possibly higher oxygen pressure can help to overcome the kinetic barriers involved in the formation of V2O5.

4.2. Surface stabilised models

In essence, our calculations predict three classes of stable thin films. At sufficiently high oxygen pressure or at sufficiently high V coverage, bulk-like V2O3+ phases are stable. These phases contain usually more oxygen than bulk V2O3, since both sides of the thin hexagonal slabs are oxygen terminated. This also implies that oxygen is located at the metal–oxide interface.

The second important category of films are the hexagonal and rectangular VO2 films, which according to our calculations are only marginally less stable than bulk VO2. Their bonding to the substrate is fairly weak, and oxygen is again located at the metal–oxide interface. The origin of the stability of these films is difficult to disentangle, because the local coordination of the V atoms is mostly octahedral as in other films and bulk VO2. Obviously the way the octahedra are linked in these structures (mainly edge sharing) is making them particularly favourable. The electronic density of states (DOS) of the r-VO2 film is shown in Fig. 8. The lower peak located between −7 and −2.5 eV contains 6 electrons and is dominated by the oxygen 2p states (the O2s states are at lower binding energies). At the Fermi-energy the V 3d states dominate. The minority Vd band is unoccupied, and the majority band is occupied by 1 electron per V atom. Since the DOS is rather large at the Fermi-level, the film might well be a Mott–Hubbard insulator at low temperature.

S-V2O3 is the third important structure, which is stable over a wide range of partial pressures at low V coverage. In this case, we find the V atoms in a trigonal coordination at the metal–oxide interface. There are some metastable phases (Pd/bulk-V2O3 – Fig. 3(a) and Pd/h-VO) which have a similar local V coordination, indicating that this coordination is particularly favourable for a V atom in contact with oxygen and the metal support. This is also confirmed by the layer resolved electronic density of states of s-V2O3 shown in Fig. 9. In a simple ionic picture the vanadium atoms donate three electrons to oxygen. But as can be seen in the layer resolved DOS the hybridization between O 2p and V 3d states is very strong (V d character at low binding energies). In a trigonal field, the five V-d bands split into three groups, two doubly degenerated E_g levels (d_x^2, d_y^2 and d_z^2, d_y, if the z-axis is orthogonal to the surface) and one A_g level (d_x^2−_y^2). All four E_g levels interact strongly with the oxygen p_z and one oxygen orbital in the xy-plane forming bonding and anti-bonding linear combinations. Also clearly visible is the hybridization

![Fig. 8. Atom resolved electronic DOS for rectangular VO2. The DOS on the V and O atoms are shown as full and dotted lines.](image-url)
including the oxygen pressure and the metal coverage much of these deficiencies can be removed, and we hope that our work will encourage similar studies in the future.

The “example” system considered here is complex and interesting on its own. To date similar studies have only been performed for the surfaces of binary systems, where only one extensive thermodynamic variable needs to be considered [20–23]. Our study is also significantly complicated by the fact that vanadium occurs in four oxidation states so that one is forced to consider varying stoichiometries. Given all these obstacles, it is remarkable how well our predictions agree with experiment: At high oxygen pressure, mostly bulk-like \( \text{V}_2\text{O}_{3+x} \) phases are stable. These films contain more oxygen than bulk \( \text{V}_2\text{O}_3 \), since both sides of the thin hexagonal slabs are oxygen terminated. When the pressure is decreased, a surface mediated \( (2 \times 2) \) \( \text{V}_2\text{O}_3 \) phase is stabilised and remains stable over a wide range of physical parameters.

A rectangular and a hexagonal \( \text{VO}_2 \) phase are expected to grow in the same pressure regime as \( s\text{-V}_2\text{O}_3 \) but at somewhat higher \( \text{V} \) coverage. These thin films differ completely in terms of structure and geometry from bulk \( \text{VO}_2 \). In fact, the models were obtained by cleaving and relaxing vanadium-monoxide along (110) or (111) planes leaving the local coordination of vanadium atoms unchanged. The lattice parameters of the novel rectangular oxide phase seem to agree with the structural parameters of the experimentally observed “flower” phase [5]. Recent experimental STM work confirms this conjecture [7]. If the partial oxygen pressure is further reduced, all phases finally decompose and \text{V} is supposed to migrate into the \text{Pd} bulk, which fully agrees with the experimental data available [5].

Finally, it seems important to highlight the procedures we have adopted in the construction of thin layers grown on a metal support. The first step was a careful investigation of bulk phases. From this study we learned how the basic building units (in our case \( \text{VO}_6 \) octahedra) can be assembled to build favourable oxides. In a second step, unsupported thin layers were investigated. They usually constitute a good starting guess for compact densely packed oxide over-layers on the metal support. The study of thin unsupported layers was

5. Conclusion

The results of our study are encouraging and demonstrate that the construction of (zero temperature) phase diagrams for binary compounds on a support is possible by means of first-principles calculations. This might actually have far fetched consequences, for instance, in heterogeneous catalysis, where structural model are nowadays often based on microscopic ultra high vacuum measurements, such as STM, and/or first-principles modelling corresponding to such conditions. By
supplemented by simulated annealing runs performed at rather low vanadium and oxygen coverage. The insight gained from these calculations was then used to construct thin supported layers at varying coverage and stoichiometry. Similar procedures should prove helpful for a wide variety of thin oxide films and metal–oxide interfaces.

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References