INTERFACIAL OXIDE LAYERS AT THE METAL–OXIDE PHASE BOUNDARY

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Received 1 November 2001

The nature of oxide phases at metal–oxide interfaces, i.e. of oxide layers in the proximity of a metal surface, is assessed by critically examining the available data in the literature. The data reveal a trend towards the formation of reduced oxide phases with lower oxidation states in the vicinity of the interface with a metal. The physical origin of these interface-stabilized oxide layers is discussed and the possible causes include strong metal–metal bonding, high oxygen affinity of the substrate metal, reduction of the interfacial strain, and the stability of two-dimensional oxide phases.

Keywords: Metal oxide; interface; metal surface; thin films.

1. Metal–Oxide Interfaces—Occurrence and Issues in Science and Technology

The interfaces between metal surfaces and oxide overlayers or substrates are of crucial importance for the macroscopic behavior of a variety of modern technological devices, such as gas sensors, solid state electronic devices, metal–ceramic composites, magnetic tunneling diodes, and a wide range of metal–oxide catalysts. Epitaxially grown thin films of oxides on dissimilar metals or on other oxide substrates are relevant to the development of novel applications in the technology for the coming decades, for example in heterostructure-based nanodevices, but they are also of fundamental scientific interest as models for oxide surfaces in general. Thin films of oxides on metals, for example, retain many of their chemical bulk properties and yet remain conductive, which is advantageous for the application of modern surface analysis techniques. Epitaxial oxide films on metal substrates may be used as supports with atomically ordered surface structure for the controlled deposition of metal particles, thus creating excellent model systems for supported metal catalysts. These model catalyst systems have been used successfully to investigate the relationship between surface structure and catalytic activity, such as particle size effects and metal–support interaction.

One class of model systems, the so-called planar model catalysts, i.e. metal particles deposited on flat oxide single crystalline surfaces, are particularly useful in the quest for novel catalysts with tailored selectivities, since they allow the preparation and characterization of well-defined metal–oxide interfaces, which have been demonstrated to play a decisive role in the performance of oxide-supported metal catalysts.

The application of thin film oxide phases in electronic device technology requires the precise control of the stoichiometry of the oxide, which is not trivial if the films are very thin and close to a metal surface. In ultrathin oxide films on metals with the oxide thickness of the order of one to several atomic layers, the stoichiometry and the oxidation state may not be identical to those of known bulk phases, because the proximity to the metal surface perturbs the electronic structure of the oxide. Interfacial oxide layers particular to and stabilized by the interface may thus be formed, and these are the subject of this paper.

There are incidental reports in the literature that oxide phases in the vicinity of a metal surface occur in a lower oxidation state than in the thermodynamically most stable oxide phase. This is conspicuous in the case of transition metal oxides, which can form
oxides with different oxidation states. Intuitively, this preference for “lower oxides” (this term will be used henceforth to designate a low oxidation state or substoichiometric oxide phases) at the metal–oxide interface may be ascribed to the electron donor properties or the “reducing character” of a metallic surface. In this paper I will examine more closely the published evidence and show that there indeed appears to be a general trend. However, the situation seems to be more complicated and I will discuss the possible driving forces for the formation of specific, sometimes metastable, interfacial oxide layers, and address the question of the terminating layer at the metal–oxide interface.

An interesting effect in the context of reduced oxides near metallic phases has been reported in the field of heterogeneous catalysis: the so-called strong metal–support interaction (SMSI) effect.\(^8\)\(^9\) It has been observed that the high temperature reduction of an oxide-supported metal catalyst leads to a catalyst surface with significantly altered chemical properties, namely reduced capabilities of \(\text{H}_2\) and \(\text{CO}\) chemisorption but increased reactivity for some catalytic reactions. This striking phenomenon has prompted a great number of studies over the last 20 years, and the SMSI effect has been found in a number of catalyst systems, where the oxide support consists of a reducible transition metal oxide. There is now converging opinion in favor of the so-called encapsulation or decoration model of SMSI:\(^10\)\(^11\) the metal particles of the catalyst in the SMSI state are (partially) covered by a reduced oxide phase. Accordingly, the oxide support in the proximity of the metal particles is reduced to a lower oxide, which tends to spread over the metal surface, thus encapsulating the metal particles. This different wetting behavior towards metals of lower transition metal oxides, as compared to the higher oxidation state oxides, has been associated with an altered interfacial energy balance.\(^12\) Also, the possible role of the metal phase in catalyzing the reduction of the oxide support at the metal–oxide-phase boundary has been suggested.\(^13\) Clearly, interfacial oxide phases must play a critical role in this oxide migration effect, and an intermediate \(\text{TiO}_1.1\) type oxide double layer has recently been proposed to encapsulate the Pt particles, as observed in a scanning tunneling microscopy (STM) study of Pt on \(\text{TiO}_2(110)\).\(^11\)

The essential characteristics of a metal–oxide interface are the geometry (structure and morphology), the electronics (electronic energy level structure), the chemistry (stoichiometry) and the adhesion strength. The last includes physical as well as chemical interactions, which sometimes lead to a distinction between reactive and nonreactive interfaces.\(^14\) A suitable approach to studying the basic aspects of interfaces at the atomic level is to use model systems, created by growing ultrathin films on single crystal substrates. With regard to the purpose of this article, namely to identify oxide phases at the metal–oxide-phase boundary, the controlled growth of thin layers of oxides on metal single crystal surfaces appears to be the most promising approach. Indeed, the most of the published work which addressed the question of structure and stoichiometry of interfacial oxide layers involved the growth of ultrathin films of oxides on metal single crystal surfaces.

Here we are interested in the atomic level structural and chemical characterization of the first few layers of oxide growth. To identify possible trends we will hence consider in the following analysis mainly data from well-defined oxide-on-metal systems, which have all been obtained under ultrahigh vacuum (UHV) conditions. In Sec. 2 of this article the available evidence in the literature will be examined to document the case, while in Sec. 3 the possible driving forces for the formation of lower oxide layers at metal–oxide interfaces in terms of interfacial interactions and lattice match considerations will be discussed. Section 4 concludes the paper with a short summary.

2. Ultrathin Oxide Layers on Metals

In this section we investigate the published information on the structure and chemical nature of very thin oxide layers in the vicinity of metal surfaces, i.e. we consider the phases of the first few monolayers (ML) of an oxide, typically from submonolayer to 1–2 ML coverages. Although only 1–2 unit cell dimensions thick, these interfacial layers are likely to determine the physicochemical properties of a metal–oxide junction in a decisive way. We concentrate here on transition metal oxides with variable oxidation states, since these provide the most interesting effects concerning oxidation–reduction behavior at the
Table 1. Oxide phases and related structures of oxide overlayers on metal substrate surfaces.

<table>
<thead>
<tr>
<th>Oxide-on-Metal System</th>
<th>Oxide/Structure</th>
<th>Methods</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_{1.77}$ (Ti$_2$O$_7$)</td>
<td>TiO$_2$</td>
<td>XPS</td>
<td>15</td>
</tr>
<tr>
<td>TiO$_{2}$ (110)-like</td>
<td>TiO</td>
<td>LEED, STM</td>
<td>16</td>
</tr>
<tr>
<td>TiO(111)-like</td>
<td>TiO</td>
<td>AES, LEED, STM</td>
<td>17</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>TiO(111)-like</td>
<td>LEED, STM</td>
<td>18</td>
</tr>
<tr>
<td>~ TiO</td>
<td>~ VO(111), 2 × 2</td>
<td>XPS, LEED</td>
<td>19</td>
</tr>
<tr>
<td>Cr$_2$O$_3$, 2 × 2</td>
<td>Cr$_2$O$_3$</td>
<td>XPS</td>
<td>20</td>
</tr>
<tr>
<td>Cr$_2$O$_3$ (111)-like</td>
<td>Cr$_2$O$_3$</td>
<td>LEED, STM</td>
<td>21</td>
</tr>
<tr>
<td>~ CrO</td>
<td>~ CrO</td>
<td>LEED</td>
<td>22</td>
</tr>
<tr>
<td>Fe$_{1-x}$O(111), 2 × 2</td>
<td>Fe$_3$O$_4$(111)</td>
<td>STM, LEED</td>
<td>23</td>
</tr>
<tr>
<td>Fe$_3$O$_4$(111)</td>
<td>Fe$_3$O$_4$(111)</td>
<td>LEED, STM</td>
<td>24, 25</td>
</tr>
<tr>
<td>CeO$_{2−x}$</td>
<td>CeO$_2$(111)</td>
<td>XPS, LEED</td>
<td>26</td>
</tr>
<tr>
<td>CeO$_2$(111)</td>
<td>CeO$_2$(111)</td>
<td>XPS, LEED</td>
<td>27</td>
</tr>
<tr>
<td>FeO</td>
<td>MgO(001)</td>
<td>SXRD</td>
<td>28</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>Al$_2$O$_3$</td>
<td>AES</td>
<td>29</td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>In$_2$O$_3$</td>
<td>UPS (He II)</td>
<td>30</td>
</tr>
</tbody>
</table>

metal interface. Most studies reported in the literature on the growth of transition metal oxides on metallic surfaces involve elements of the first period of the periodic table. These results thus form the bulk of the material examined here, but some related data on other oxides such as ceria or group III oxides are also included. Table 1 gives an overview of the results from relevant oxide-on-metal UHV growth studies, together with the experimental methods employed, the proposed oxide phases at the interface ($\Theta_{\text{oxide}} \leq 1$–2 ML), and the oxide phases observed for thicker film growth ($\Theta_{\text{oxide}} > 2$ ML). After oxide deposition onto substrates at elevated temperatures and/or postannealing, most oxide overlayers display ordered structures. These are indicated in Table 1 for commensurate lattices in terms of their surface unit mesh [e.g. 2 × 2]; in the case of incommensurate structures the most closely resembling oxide plane is given [e.g. TiO(111)-like or FeO(111)].

Although some of the proposed stoichiometries and structures at low oxide coverages cited in Table 1 have to be regarded with caution at the present time, a common trend towards the formation of lower oxides at the oxide–metal interface is apparent. To obtain a more detailed picture of the characteristic oxide phases and their properties at the different interfaces, some selected systems are next investigated more closely, in the form of individual case studies.

2.1. Titanium oxide on Pt(111)

Boffa et al. have studied titanium oxide films grown by vapor phase deposition of Ti metal followed by oxidation in $10^{-6}$ Torr O$_2$ at 500–800°C on Pt(111), with a variety of surface science spectroscopies. By X-ray photoelectron spectroscopy (XPS) they identified a Ti$_4$O$_7$ phase at 1–1.5 ML coverages and a stoichiometric TiO$_2$ layer for higher coverages (5 ML).
The latter gave a complex LEED pattern with a \((\sqrt{43} \times \sqrt{43})R7.6^\circ\) unit cell, which has been tentatively associated with a (111)-like crystal face of the TiO\(_2\) rutile structure. The reduced Ti–oxide phase at lower coverages also displayed an ordered overlayer structure in LEED and STM, which the authors have ascribed to a TiO\(_2\)(110) matrix with O anion defects. Boffa \textit{et al.} obtained indications, by angle-resolved XPS, that the reduced Ti\(^{3+}\) species are concentrated at the oxide/Pt(111) interface; this is a relevant observation in the present context.

A series of complex LEED patterns, depending on the exact Ti coverage and annealing conditions, have also been reported at around 1 ML coverage of TiO\(_x\) on W(110), by Herman \textit{et al.} Some of the structures have been interpreted in terms of coincidence lattices, and an epitaxially grown distorted TiO(111) layer has been proposed.

It is worth mentioning that the oxidation of Pt\(_3\)Ti alloy single crystal surfaces follows reportedly a three-stage process:\(^3\) initially, a compact epitaxial TiO monolayer is formed at the metallic surface; further oxidation causes the formation of a multilayer of a TiO\(_{1.2}\) defect phase; and, finally, under severe oxidation conditions a thick rutile type TiO\(_2\) overlayer is formed. Therefore, a lower oxide layer is also indicated here at the metal–oxide interface.

2.2. Vanadium oxide on Pd(111)

The layer-dependent evolution of thin films of vanadium oxides on Pd(111), grown by reactive evaporation of V metal in an oxygen atmosphere, has been thoroughly investigated in the laboratory of this author, using a variety of techniques, including high resolution XPS with synchrotron radiation, LEED, STM and high resolution electron energy loss spectroscopy (HREELS).\(^3\) At submonolayer coverages, a layer of a specific interface-stabilized oxide phase with a formal V\(_2\)O\(_3\) stoichiometry, yet a very different structure as compared to the known V\(_2\)O\(_3\) bulk phase, is formed. It constitutes a 2 \times 2 honeycomb structure as detected by STM and LEED [Figs. 1(a) and 1(b)]. The structural details of this so-called surface–V\(_2\)O\(_3\) phase have been revealed by first principles density functional theory (DFT) calculations and simulations of STM images,\(^3\) and a structural model is shown in Fig. 1(d). An important feature of this interfacial oxide phase is the V termination at the Pd interface (while oxygen atoms form the surface to the vacuum), which is caused by the strong V–Pd bond.\(^3\) The proximity and bonding of the V atoms to the Pd surface causes an XPS V 2p core level shift of \(\sim 1\) eV to lower binding energy with respect to bulk type V\(_2\)O\(_3\) [Fig. 1(c)], which is also predicted by DFT but which has led previously to the erroneous assignment of this phase to a VO stoichiometry (this illustrates the danger of simplistic XPS energy shift interpretations). The growth of a second layer of V–oxide on top of this surface–V\(_2\)O\(_3\) layer is energetically unstable. This is most intuitively understood in terms of the so-called layer dipole rule, which states that a polar surface cannot support further film growth because the overall dipole of the film would diverge. For V–oxide growth on Pd(111) a sudden transformation from surface–V\(_2\)O\(_3\) to a VO\(_2\) type phase takes place on further V–oxide deposition.\(^3\) The collapse of surface–V\(_2\)O\(_3\)
is accompanied by a radical change at the oxide–Pd interface, which transforms from Pd–V–O into a Pd–O–V stacking sequence. Two different VO$_2$ type thin film phases are energetically possible and have been experimentally observed, with a rectangular incommensurate and a hexagonal commensurate lattice structure with respect to Pd(111). Notice that these latter ultrathin V–oxide layers are again particular to the interface and bear no resemblance to a bulk rutile type VO$_2$ phase. The rectangular VO$_2$ phase is slightly more stable than the hexagonal VO$_2$, but only the latter can support further growth because the rectangular VO$_2$ layer has a nonzero dipole moment (see above). Eventually, the V–oxide film converges via another precursor phase to a bulk type V$_2$O$_3$ structure for a film thickness $> 3$–4 ML; the latter is the stable V–oxide phase for thick films under experimental UHV type growth conditions. The bulk type V$_2$O$_3$ layer is O-terminated at both interfaces, although the interface to the vacuum (the surface) may occur in two different configurations.

This brief summary of the evolution of surface structures of V–oxides on Pd(111) with increasing film thickness shows the extremely complicated situation which can occur at the interface of a metal to an oxide system with several stable oxidation states. For the V–oxide/Pd(111) interface the oxidation state of the V atoms appears to oscillate between $3^+$ (surface–V$_2$O$_3$), $4^+$ (VO$_2$), and $3^+$ (bulk V$_2$O$_3$) again. From a different viewpoint, however, the surface–V$_2$O$_3$ layer may be regarded as a lower oxide phase despite its formal stoichiometry: the oxygen coordination of the V atoms, which are partly bonded to surface Pd atoms, is distinctly reduced as compared to the typical octahedral O coordination of bulk vanadium oxides. We emphasize again that the surface–V$_2$O$_3$ phase derives its stability from the V termination at the interface and the concomitant strong V–Pd bonding.

Two reports of V–oxide growth by Kishi et al. have suggested that epitaxial VO type 2 $\times$ 2 overlayers are formed at 1–2 ML coverages on Ni(110) and Cu(100) surfaces. These propositions were based on a negative chemical shift of V 2p core level XPS peaks of $-0.6$ eV with respect to bulk V$_2$O$_3$. In view of the results discussed above, it is more likely that this chemical shift is the result of the metal–metal bonding of an interfacial oxide of the type described above, rather than being due to oxide overlayers with VO stoichiometry, which are energetically unstable.

2.3. Chromium oxide on Pt(111)

XPS spectra of the Cr 2p core levels of Cr–oxide deposited on Pt(111) suggested the presence of both Cr$^{3+}$ and Cr$^{2+}$ species in 1–2 ML-thick overlayers, whereas only Cr$^{3+}$ was indicated for thicker oxide films. The first two layers of Cr–oxide on Pt(111) display an ordered 2 $\times$ 2 LEED pattern, while a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure is established at higher coverages, i.e. $> 3$ ML. Zhang et al. suggested a cubic spinel Cr$_3$O$_4$ phase for the low coverage regime and emphasized the stabilizing role of the interface to the Pt for this metastable oxide phase. The termination of the interfacial oxide layer towards the metal surface could not be determined in this study, and it is uncertain whether oxygen or chromium constitutes the first atomic layer above the Pt surface. The higher coverage Cr–oxide film has been identified as an epitaxial Cr$_2$O$_3$ layer with its (0001) face parallel to Pt(111). The epitaxial growth of Cr$_2$O$_3$, the only stable chromium oxide bulk phase, is facilitated by the close lattice match between the $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer and the Pt(111) substrate (lattice misfit $\sim 3\%$).

2.4. Iron oxide on Pt(111)

There is convincing evidence in the literature that the first monolayer of iron oxide on Pt(111) is of a cubic FeO structure. Galloway et al. have described this layer as a hexagonal bilayer of FeO(111) rotated by $\sim 0.6^\circ$ with respect to the Pt lattice. The lattice mismatch of $\sim 12\%$ between FeO and Pt gives rise to a Moiré type pattern in the STM, and from the analysis of the Moiré superlattice and the rotational mismatch the iron oxide lattice constant has been derived to 3.09 Å, which is slightly expanded with respect to the bulk value of FeO (3.04 Å). Figure 2 shows a model of the FeO(111) bilayer on Pt(111), as proposed by Galloway et al. and adapted by Ritter et al. The FeO bilayer is iron-terminated at the interface to the platinum and has an oxygen-terminated layer at the outer surface. Ranke et al. have observed four different coincidence structures of a similar type of unreconstructed FeO(111) films with somewhat different lattice relaxations as a function of coverage up to 2 ML. After
completion of 2 ML, three-dimensional islands of Fe$_3$O$_4$(111) started to grow, which were transformed into α-Fe$_2$O$_3$ by higher pressure oxidation conditions. The small lattice mismatch between the (111) oxygen planes of Fe$_3$O$_4$ and FeO facilitates the epitaxial growth of the Fe$_3$O$_4$ islands, as observed. The formation of Fe$_3$O$_4$ instead of Fe$_2$O$_3$, as the bulk phase diagram would predict, has been attributed to kinetic effects.

Although FeO in bulk form is not an equilibrium structure at room temperature, it has been argued that the interfacial interactions with the Pt substrate provide sufficient energy for the stabilization of FeO in ultrathin film form. It is interesting to note that the FeO bilayer as shown in the model of Fig. 2 is a polar surface, and thus prone to instability upon further growth. Ritter et al.\textsuperscript{25} have realized this and rationalized the observed growth of a second layer of FeO on top of the first one by the compensating effect of an image dipole in the Pt substrate.

2.5. Cerium oxide on Rh(111)

The growth of cerium oxide thin films on Rh(111) has been studied in our laboratory in Graz as a function of film thickness using photoelectron spectroscopy and LEED.\textsuperscript{26} Figure 3(a) shows a collection of Ce 3d XPS spectra of cerium oxide films on Rh(111), with increasing film thickness (in ML) from bottom to top. The Ce 3d spectra display a complicated manifold of peaks due to spin–orbit and final state effects,\textsuperscript{41} and the presence of both Ce$^{3+}$ and Ce$^{4+}$ species in the oxide layers. However, using the spectral structure at ~916 eV binding energy, which is solely due to Ce$^{4+}$ species, in combination with the total area of the Ce 3d XPS structure, the relative amount of reduced Ce$^{3+}$ species can be estimated.\textsuperscript{26} The percentage numbers of Ce$^{3+}$ are given in Fig. 3(a), whereas the $x$ in CeO$_{2-x}$ is plotted against the oxide film thickness in Fig. 3(b), $x = 0$ meaning stoichiometric CeO$_2$. Clearly, at low coverages substantially reduced CeO$_{2-x}$ overlayers are observed and a fully oxidized CeO$_2$ film can only be obtained for film thicknesses $\geq 7$ ML. LEED and STM measurements indicate that the CeO$_{2-x}$ films grow in the form of epitaxial crystallites and that the reduced oxide layers are characterized by oxygen defect phases rather
than a Ce₂O₃ type phase.⁴² The observations on the Ce–oxide-on-Rh(111) system are in agreement with those of Alexandrou and Nix²⁷ on ceria overlayers on Pd(111), who reported that only reduced cerium oxide layers could be obtained for thin films, i.e. close to the interface to the metal.

2.6. Other oxides

Most oxide–metal systems of interest in this paper concern transition metal oxides, which can occur in variable oxidation states. However, there are incidental reports that reduced oxide phases might occur on seemingly single-valent oxide overlayers. Ko and Gorte,²⁹ for example, suggested that suboxides of alumina could be formed on a Pt foil support after oxidation of deposited Al metal, the evidence being based on Auger electron spectroscopy. On oxidizing a NiIn(0001) alloy single crystal surface Blyth et al.³⁰ have obtained indications, from In 4d photoemission spectra, that an In suboxide, possibly In monoxide, might be formed at the metal–oxide interface, below a stoichiometric In₂O₃ overlayer.

An interesting interfacial oxide phase has been reported recently between an Fe(001) substrate and a MgO overlayer.²⁸ This system is of interest in connection with the realization of tunneling magnetoresistance junctions, because MgO can be grown epitaxially on Fe(001), thus providing a monocrystalline barrier in the Fe/MgO/Fe(001) system. Meyheimer et al. have applied surface X-ray diffraction (SXRD) to study the growth of MgO on Fe(001) and found an FeO-like interface layer between the substrate and the MgO structure.²⁸ This intermediate layer generates a structurally “graded” interface which may be beneficial to the epitaxial layer-by-layer growth of the MgO.

3. The Physical Origin of Lower Oxide Layers at Metal–Oxide Interfaces

The data investigated in Sec. 2 demonstrate that lower oxide phases are frequently encountered at the interface of an oxide and a metal. These lower oxide layers derive their stability from the chemical interactions with the substrate atoms at the interface and/or from geometry-related effects (i.e. lattice matching), which reduce the interfacial strain and thus lower the elastic stress energy. Moreover, quasi-two-dimensional oxide thin film phases may become stable under particular growth conditions.

The chemical interactions determine the terminating layer of the oxide at the interface. In the two well-documented cases, FeO/Pt(111) and surface–V₂O₅/Pd(111), the metal atoms of the oxide are proposed to be located at the interface. For vanadium oxide on Pd(111) the DFT calculations of Kresse et al.³⁵ emphasize the strong tendency of V atoms to heterocoordinate with Pd surface atoms at low oxide coverages. This tendency to metal–metal bonding is expected to follow the trends of alloy formation or of dissolution of the oxide overlayer metal into the bulk of the substrate metal. Alloying has been observed on heating in the Pd–V system, and indeed Kresse et al. predict that it is energetically favorable for V adatoms on Pd(111) to dissolve into the bulk or to form a Pd₃V surface alloy. For titania on Pt(111) Boffa et al.¹⁵ have also observed dissolution of Ti into the Pt substrate at moderate temperatures (500°C). This would suggest that the favorable Ti–Pt coordination leads to a Ti layer at the titania–Pt interface, and Boffa et al. have proposed, based on angle-resolved XPS data, that the reduced Ti³⁺ species are in fact concentrated at the metal–oxide interface. This was in line with the earlier Hartree–Fock calculations of Pt on TiO₂ by Horsey,⁴³ who emphasized the importance of direct Ti–Pt bonding between the reduced titania and Pt particles in his attempt to rationalize the SMSI effect on titania-supported Pt catalysts. Cerium forms readily surface alloys on Rh(111),²⁶ and it is therefore suggestive that Ce–Rh bonding is also important in stabilizing the reduced cerium oxide layer at the Rh interface.

The case of FeO on Pt(111) appears to be more puzzling. On the one hand, Galloway et al.²⁴ reported that adsorbed Fe diffuses into Pt upon heating to moderate temperatures (≤ 500°C) and the model of Fig. 2 shows an Fe layer in contact with the Pt surface, indicating Fe–Pt bonding. On the other hand, Ranke et al.³⁹ have observed a series of higher order coincidence structures of FeO on Pt(111) with varying lattice constants and small rotational misalignment angles with respect to the substrate’s high symmetry directions. This is reminiscent of the phenomenon of rotational epitaxy⁴⁴–⁴⁶ and indicates weak coupling of the overlayer to the substrate. Accordingly, the contribution of the direct
Fe–Pt bonding to the stability of the FeO interfacial layer should be moderate at most. We recall at this point that for ~1 ML coverage of vanadium oxide on Pd(111) a metastable incommensurate VO$_2$ type phase has been detected, which becomes unstable again upon further oxide growth. The DFT calculations have established that this phase is a stable thin film oxide phase, which is weakly coupled to the substrate. It has a similar local V–O coordination to the known VO$_2$ bulk oxide but a very different structure. Note that a thin layer of bulk type VO$_2$ is unstable according to DFT. Thus, some oxide phase diagrams in the ultrathin film limit may allow for the existence of oxide phases which have no correspondence in the respective bulk phase diagrams. It is conceivable that a similar situation applies to the iron oxide system.

Oxygen-terminated V–oxide/Pd interfaces become stable for $\geq$ 1 ML oxide coverages, but for more reactive metal substrates they are likely to form also at the early growth stage. Diebold et al. have studied the systems “inverse” to the ones considered here, namely metal overlayer growth on TiO$_2$ single crystal surfaces, and have found a correlation between the affinity of the metal towards oxygen and the heat of oxide formation of the overlayer metal. Similarly, Peden et al. have concluded earlier, for metals deposited on an oxidized W surface, that the interfacial reactivity follows the trend of the heat of formation of the oxides of these metals. The tendency to form oxygen-terminated interfaces in the case of oxide overlayers on metals presumably follows the same trend.

For the reactive interfaces the metal may act as an electron donor in the classical chemical sense and the charge transfer from the metal to the oxide will be directly responsible for the reduction of the oxide and the formation of the lower oxide phases. The strength of the oxidation–reduction at the interface is related to the reactivity of the metal towards oxygen. The relative oxygen affinity

$$\log p_{O2} = -\Delta G_f / RT$$

may be used as a measure to gauge the interface reactivity: a metal will reduce an oxide whose affinity is smaller than its own.

Recently, Jennison and Bogicevic have calculated two oxygen-layer aluminium oxide films on Al(111) and Ru(0001) surfaces and found that the preferred interface between the oxide film and the substrate consists of a 1 x 1 chemisorbed oxygen layer. Since these calculations were aimed at modeling the structure of thin alumina films on NiAl alloy single crystal surfaces, the film thickness was constrained to two layers of oxide and the Al/O ratio was kept stoichiometric. This situation is thus more comparable to the $\geq$ 2 ML case of vanadium oxides on Pd, where also oxygen-terminated interfaces have been identified, rather than being typical of the initial oxide-on-metal growth.

The formation of a metastable 2 x 2 layer of Cr$_3$O$_4$ at the chromium oxide/Pt(111) interface has been discussed by Zhang et al. in terms of lattice matching considerations. They pointed out that the Cr$_3$O$_4$ and Pt have the same fcc structure; however, since the subsequently formed Cr$_2$O$_3$ (0001) structure is also well matched to the Pt(111) substrate, this argument alone seems insufficient to explain the stabilization of the Cr$_3$O$_4$ interfacial layer. Zhang et al. mentioned further that Cr$_3$O$_4$ may be stabilized by the Pt(111) substrate; in the context of the present discussion this would point to an important role of the Cr–Pt bonding. The lattice matching argument is clearly an important one for the vanadia/Pd(111) system. Of the two metastable VO$_2$ thin film phases (~ 1 ML coverage), only the commensurate lattice-matched hexagonal VO$_2$ phase can support the growth of the V$_2$O$_3$ bulk precursor phase. The formation of particular interfacial oxide layers which provide a better lattice matching to the substrate than stable bulk oxide structures may be beneficial to the total energy of the system in reducing the interfacial strain energy. If reasonable lattice matching can be achieved with the subsequently growing stable bulk type oxide phases, a structurally “graded” interface with minimized interfacial strain and low total energy may be obtained. This seems to be the driving force for the formation of the FeO monolayer at the MgO/Fe(001) interface, as reported above.

The lower oxide phases at the oxide–metal interfaces tend to be metastable with respect to the oxide growth process. If the oxide layer derives its stability from direct overlayer–substrate bonding interactions, only the first monolayer will be favorable and subsequent layers, which cannot be in contact with the metal, will not be stabilized; they will return to their thermodynamical equilibrium (bulk) structures. In cases where the oxide phase diagram in the
ultrathin layer limit provides for particular quasi-
two-dimensional thin film phases, these will become
inherently unstable with the loss of low dimension-
ality and disappear for thicker films. Another cause
of metastability is instability with respect to further
growth. As mentioned in Sec. 2, polar oxide surfaces
cannot support unlimited growth, because the sur-
face energy diverges with the increasing total dipole
moment, thus providing a self-limitation of the layer

thickness.

The oxygen pressure during oxide thin film prepara-
tion or interface studies has not been considered
thus far in this article. Most studies cited in this
study have been performed under UHV conditions
(O$_2$ partial pressure typically $10^{-7}$-$10^{-5}$ mbar), for
reasons of precise experimental control, and the vari-
ation of the oxygen pressure has not been investi-
gated in great detail or in a wide range. Clearly,
the oxygen pressure is an important thermodynamic
variable in the oxide–metal interface formation pro-
cess, and more work has to be devoted to studying
the stability of interfacial oxide phases at higher
pressure. Kresse et al.\textsuperscript{35} have studied theoretically
the stability of the various vanadium oxide phases
on Pd(111) for a varying chemical potential of the
oxygen. The interfacial surface–V$_2$O$_3$ oxide layer
(Fig. 1) is remarkably stable over a wide range of oxy-
gen pressures, indicating that the low pressure UHV
studies do give important insights into the nature
of metal–oxide interfaces. However, a single layer of
V$_2$O$_5$ is also predicted by DFT to be stable in the
higher, but still UHV-compatible, oxygen pressure
range, but this has yet to be observed experiment-
ally. Whether this is due to a kinetic limitation
will have to await experiments performed at higher
oxygen pressures.

The preparation of metal–oxide interface systems
involves exposure of the metal surface to oxygen, in
one way or another. For the more reactive metal
surfaces the result is likely the formation of a thin
layer of surface oxide, onto which the desired oxide
layer is deposited. The MgO/Fe(001) system with its
FeO interlayer\textsuperscript{28} as discussed above may be regarded
as an example of this. But also on the surfaces of the
less reactive metals of the second and third periods of
group VIII of the periodic table, which are most rele-
vant in catalysis, oxygen penetration into the surface
has been observed under oxide overlayer prepara-
tion conditions.\textsuperscript{53} The presence of subsurface oxygen

or oxygen dissolution in the surface near region of
the substrate metal may well have an influence on the
formation of interfacial oxide layers. The influence
of the oxygen solubility in the substrate metal on the
metal–oxide interface phase diagram has not been
addressed so far. One way of testing the impor-
tance of this effect is to investigate the growth of the
same oxide overlayer system on different metal sub-
strates. A study of vanadium oxide overlayer growth
on Rh, which has a higher affinity to oxygen than
Pd, with the purpose of comparing it to the vana-
dium oxide/Pd(111) system, is presently underway
in our laboratory.

4. Summary

In this paper I have investigated the published
evidence supporting the notion of lower-oxidation
state oxide phase formation at metal–oxide inter-
faces. The results considered here are those of well-
characterized UHV studies of oxide-on-metal growth,
which provide the most detailed atomic scale informa-
tion on the nature and structure of oxide–metal
interfaces. The data confirm the trend that lower
oxide phases are formed in the vicinity of the in-
terface with a metal surface. The physical origin
of these interface-stabilized oxide layers is discussed
in terms of the competition between metal–metal
bonding and reactivity towards oxygen at the inter-
face, lattice-matching geometry considerations, and
two-dimensional phase diagrams.

The implications of interfacial oxide layers in
science and technology are far-reaching. The lower
oxide phases in the ultrathin film limit have an im-
portant influence on the physicochemical properties
of thin layer oxide structures, which will become in-
creasingly important in future technologies. They
determine the morphology of the interface with a
metal and the electronic transport processes across
the interface, which are both relevant to the perfor-
mance of tunneling and other electronic devices. In
the field of catalysis, the interfacial oxide region be-
tween the metal and the oxide component plays a
significant role for the morphology and the overall
chemistry of oxide-supported metal catalysts.

Acknowledgments

This work has been supported in part by the Aus-
trian Science Foundation. F. P. N. acknowledges
support by the Österreichische Forschungsgemeinschaft and the Dr.-Heinrich-Jörg-Stiftung of the Karl-Franzens-Universität Graz. It is a pleasure to thank Prof. Gabor A. Somorjai, University of California, Berkeley, for the many interesting discussions and for his excellent hospitality at Berkeley, where this manuscript was prepared. Michael G. Ramsey and Svetlozar Surnev of the Karl-Franzens-Universität Graz are acknowledged for a critical reading of the manuscript.

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