Metal Adatoms and Clusters on Ultrathin Zirconia Films

Joong Il Jake Choi, Wernfried Mayr-Schmöller, Ilaria Valenti, Paola Luches, Josef Redinger, Ulrike Diebold, and Michael Schmid*

1. INTRODUCTION

Metal clusters supported on zirconia (ZrO₂) and metal–zirconia interfaces are interesting for heterogeneous catalysis and important for solid oxide fuel cells (SOFCs) and oxygen gas sensors. In SOFCs and zirconia-based gas sensors, zirconia (with dopants such as yttria, then named yttria-stabilized zirconia, YSZ) is used as an electrolyte. Here, zirconia is sandwiched between the cathode and anode materials, which are often porous metals. These applications rely on the favorable properties of zirconia: high mechanical strength, high melting point (2983 K), electronic insulation with a large band gap (≈5 eV) even in doped form, and dopant-induced oxygen ion conductivity at high temperature (≥600 °C). Despite the importance for applications, atomic-scale studies of zirconia surfaces and metal–ZrO₂ interfaces are very rare, mainly because most conventional surface sensitive probing techniques require electronic conductivity.

In order to overcome this shortfall, ultrathin zirconia films were grown by reactive evaporation of Zr onto Pt surfaces. However, evaporation of Zr in ultrahigh vacuum (UHV) is difficult, and such ZrO₂ films are often inhomogeneous. We have followed an alternative approach and grown ultrathin ZrO₂ films by oxidation of Pt₃Zr(0001) and Pd₃Zr(0001) alloys. These two Zr alloys have the same Ni₃Ti-type D0₂₄ structure. They exhibit high thermal and chemical stability (so-called Engel–Brewer alloys) and strong chemical order, which slows down diffusion. Therefore, oxidation of the alloy constituent Zr is slow, which is beneficial for the formation of a well-ordered oxide layer. Oxidation of such Zr alloys followed by annealing in UHV results in a single O₃Zr = 350 ± 2 pm on Pt₃Zr(0001) and Pd₃Zr(0001), compared to roughly 360 pm for c-ZrO₂(111). Atomically resolved scanning tunneling microscopy (STM) images could be obtained on these ultrathin ZrO₂ films, and they were studied in detail by X-ray photoelectron spectroscopy (XPS).

Despite their similar structures, there are differences between the ZrO₂ films on Pt₃Zr and Pd₃Zr, mostly caused by the...
binding mechanism of the ultrathin zirconia films to the substrate. As is shown in Figure 1, the oxide films are distorted with respect to perfectly cubic ZrO$_2$(111), which would show planar O and Zr layers. The degree of distortion is related to the surface composition of the substrate. During oxidation of Pt$_3$Zr, Zr is liberated from the alloy, which results in at least one Pt layer at the top of the substrate. The Pt layer can be identified as such because it is reconstructed in the same way as pure Pt(111). This reconstruction is based on dislocations and would not be possible for an alloy like Pt$_3$Zr, which exhibits strong chemical ordering; this would keep the metal layers in registry with each other. Diffusion in Pd$_3$Zr is easier at the high temperatures needed for forming a well-ordered oxide film. Thus, on Pd$_3$Zr the substrate layer below the oxide is roughly stoichiometric; i.e., both Pd and Zr are present at the interface with the oxide. The existence of Zr in the uppermost substrate layer provides the possibility for strong O$_{ox}$-Zr$_{sub}$ bonds on Pt$_3$Zr/ZrO$_2$ and O$_{ox}$-Zr$_{sub}$ bonds on ZrO$_2$/Pd$_3$Zr. Figure 1. Side view of a trilayer zirconia film grown on (a) Pt$_3$Zr(0001) and (b) Pd$_3$Zr(0001) (c). The thick blue lines between oxide and substrate show the main bonding mechanism: Zr$_{ox}$-Pt$_{sub}$ bonds on Pt$_3$Zr/ZrO$_2$ and O$_{ox}$-Zr$_{sub}$ bonds on ZrO$_2$/Pd$_3$Zr. Figure based on DFT calculations for small model cells. 

2. EXPERIMENTAL AND COMPUTATIONAL DETAILS

2.1. Experimental Setup. All experiments were performed in two interconnected UHV chambers: one mainly for sample preparation and the other for STM, Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED). Both chambers have a base pressure below 10$^{-10}$ mbar. The ultrathin ZrO$_2$ films were prepared by oxidation of Pt$_3$Zr(0001) and Pd$_3$Zr(0001) samples and postannealing; the detailed preparation procedures are documented in refs 9 and 10, respectively. Metals were deposited with the sample at room temperature unless otherwise noted. We used evaporation from electron-bombarded rods to deposit Fe, Ni, and Pd; the coinage metals Ag and Au were evaporated from Mo crucibles. During deposition, a voltage of +1.5 kV was applied to a tube electrode at the orifice of the evaporators in order to prevent impingement of fast ions on the sample, which could otherwise damage the surface and modify the growth mode. Deposition rates were calibrated with a quartz-crystal microbalance (QCM) put in place of the sample before and after deposition. In addition, the deposition rate of Au was determined by submonolayer deposition on Pt$_3$Zr(0001) and measuring the area fraction covered by the one-dimensional (1D) Au islands observed by STM. The amount of deposited material is given in units of monolayers (ML), defined with respect to the 0.35 nm lattice of the ZrO$_2$ trilayer film; i.e., 1 ML = 9.4 × 10$^{18}$ atoms/m$^2$.

STM measurements were performed at room temperature with electrochemically etched, sputter-cleaned W tips. The bias voltages given are sample voltages $V_s$; positive values correspond to tunneling into unoccupied states. Most images have been taken at $V_s$ ≈ ±0.5—1 V and tunneling currents of 0.1—0.3 nA. At voltages below ≈2 V, usually the main influence of voltage and current on the appearance of the images is improvement of tip stability with larger distance (higher absolute value of the voltage), at the cost of reduced resolution. Also, the influence of the tunneling parameters on the cluster height distributions is small; nevertheless the voltage values are given in all height distributions. For better statistics, the cluster height distributions were obtained from larger scanning areas than the ones shown in the images.

2.2. Determination of True Cluster Heights and Contact Angles. For the analysis of our results, it is important to know the actual (geometric) thickness of the metal clusters, which differs from their apparent height measured by STM.

Figure 2. (a) Imaging of an oxide and an oxide-supported cluster by STM. The apparent height of the oxide $h_{app,ox}$ is much lower than its true height; thus the apparent cluster heights $h_{app,cl}$ are too large. (b) Measured heights of Ag clusters (blue squares) and correspondence to estimated cluster heights assuming an apparent height of 550 pm for the first Ag layer and an Ag(111) interlayer distance of 236 pm (red line). (c) A cluster with contact angle $\alpha$ and height $h$, assuming its shape can be approximated by a truncated sphere.
Having accurate thickness values is especially important for the determination of contact angles. In the following we assume that the contact area beneath the metal cluster is sufficiently large, so that the tunneling resistance of the cluster–oxide–substrate barrier is negligible compared to that between the tip and the cluster. Here we assume that the electrons can be first accommodated in the cluster, and then they easily transverse the oxide beneath due to the large base area of the cluster. In this case, the additional electrical resistance between the cluster and the substrate can be neglected. This picture is inappropriate for clusters with very small thicknesses, where the tunneling electrons may travel ballistically through the cluster and oxide into the substrate. (In that case, the electrons also feel the oxide as a barrier, which means that the cluster would appear lower.) For sufficiently large clusters, we further assume that the uppermost terrace is large enough that its apparent height is not limited by getting blurred due to its final lateral extension. With these assumptions, Figure 2a shows for a metal cluster with monolayer height that

\[ h_{\text{tip-sub}} + h_{\text{app,ox}} + h_{\text{app,cl}} = d_{\text{ox-sub}} + d_{\text{ox}} + d_{\text{cl-ox}} + h_{\text{tip-cl}} \]

Here, \( h_{\text{tip-sub}} \) and \( h_{\text{tip-cl}} \) are the heights of the tip above the uppermost atoms of the substrate and cluster respectively, while \( h_{\text{app,ox}} \) and \( h_{\text{app,cl}} \) denote the apparent height of the oxide above the substrate and cluster above the oxide as shown in STM images. The \( d \) symbols refer to geometric (true) interlayer distances: \( d_{\text{ox-sub}} \) between the lowest layer of the oxide and the substrate; \( d_{\text{ox}} \) between the uppermost and lowest layer of the oxide, and \( d_{\text{cl-ox}} \) between the bottom layer of the cluster and the uppermost layer of the oxide. For a cluster with a thickness of \( n_{\text{cl}} \) monolayers, we have to add the thickness of the additional metal layers, \((n_{\text{cl}} - 1)d_{\text{ML,cl}}\) to the apparent height, where \( d_{\text{ML,cl}} \) is the interlayer distance in the cluster. It then follows from eq 1 that the apparent height of a cluster with a thickness of \( n_{\text{cl}} \) monolayers is given by

\[ h_{\text{app,cl}} = d_{\text{ox-sub}} + d_{\text{ox}} + d_{\text{cl-ox}} + h_{\text{tip-cl}} - h_{\text{tip-sub}} - (n_{\text{cl}} - 1)d_{\text{ML,cl}} \]

For our analysis of Ag clusters, we assume Ag(111) layers (see below, \( d_{\text{ML,cl}} = 236 \) pm), the \( d_{\text{ox-sub}} \) and \( d_{\text{ox}} \) interlayer distances from ref 9 as given in Figure 2a, and an Ag–oxide distance slightly larger than the oxide–substrate distance (\( d_{\text{cl-ox}} \approx 270 \) pm). With the further assumption of \( h_{\text{tip-cl}} - h_{\text{tip-sub}} \approx 20 \) pm based on STM observations of Ag on pure Pt(111)\(^{14}\) and an apparent oxide height of \( h_{\text{app,ox}} \approx 180 \) pm at \( V_e = \pm 1 \) V, we obtain an apparent height of \( \approx 550 \) pm for a cluster consisting of a single Ag(111) monolayer imaged at \( V_e = \pm 1 \) V. The calculated height as a function of cluster thickness \( n_{\text{cl}} \) is shown as a red line in Figure 2b, together with experimental values for the apparent height of Ag clusters from actual STM data. The number of layers corresponding to the experimental cluster heights are not known, but we can find a reasonable match between the calculated and experimental apparent heights only if the correspondence is as shown in Figure 2b. The agreement is best for large clusters, while small clusters appear lower than calculated. This observation perfectly fulfills our expectation mentioned above, that small clusters should be imaged with lower apparent height than calculated by eq 2 for two reasons: the height profile over small terraces at the top gets smeared out and thus appears lower, and the influence of tunneling through the oxide film cannot be neglected.

In summary, we can use eq 2 or Figure 2b to convert the measured (apparent) cluster height \( h_{\text{app,cl}} \) into the true (geometrical) cluster thickness \( h \). We can then determine the contact angle \( \alpha \) from the height distribution and the amount of material in the clusters, as determined from the deposited amount and the cluster density. This procedure is explained in detail in ref 15 and assumes that the clusters have a sufficiently large volume and uniform shape as shown in Figure 2c. In the current work, only Ag clusters fulfill these assumptions; the other materials form clusters that are too small or do not show a three-dimensional (3D) shape.

2.3. Computational Details. The DFT calculations were done using the Vienna Ab initio Simulation Package (VASP), which employs the projector augmented wave formalism using pseudopotentials. As the proper treatment of dispersion effects is important for the description of the alloy–zirconia interface, the so-called optB86b functional was used. This functional improves the generalized gradient approximation (GGA)\(^{15}\) by accounting for the van der Waals interactions according to the formalism of Dion.\(^{20}\) Generally, an energy cutoff of 400 eV and fine Γ-centered k-point grids generated according to the Monkhorst–Pack\(^{21}\) scheme were used to ensure electronic convergence. All structures were relaxed until the residual forces were below 0.01 eV/Å.

To gain a deeper understanding of the growth of metals on zirconia surfaces, the adsorption of these adatoms on both the surface of monoclinic bulk ZrO\(_2\) and the surface of ultrathin films were calculated. Zirconia exhibits two phase transitions with increasing temperature, from the monoclinic (m) ground state to the tetragonal phase at \( \approx 1440 \) K and to the cubic (c) phase at \( \approx 2640 \) K. Our structure models for m-ZrO\(_2\) are based on the lattice parameters determined by DFT (Table 1), which agree well with experimental data.\(^ {22}\) According to both Christensen et al.\(^ {23}\) and our own calculations, for m-ZrO\(_2\) the (111) surface is the most stable one; it is a distorted version of c-ZrO\(_2\)(111), the lowest-energy surface of the cubic phase. Like c-ZrO\(_2\)(111), the m-ZrO\(_2\)(111) structure can be thought of as charge-neutral ZrO\(_2\) trilayers parallel to the surface [Figure 3a]. The unit cell of m-ZrO\(_2\)(111) [Figure 3b] contains \( (2 \times 2) \) formula units per trilayer. The thickness of the slab was four O–Zr–O trilayers, which is sufficient according to both ref 24 and our own findings; the bottom two ZrO\(_2\) trilayers were kept fixed at their bulk positions. A \( 5 \times 5 \times 1 \) Γ-centered k-point mesh consisting of 13 irreducible k-points was used. As is usual for insulators, DFT calculations underestimate the band gap (3.6 eV with the present functional; experimental values are around 5–5.7 eV\(^ {25}\)). This will influence the energy range where metal and ZrO\(_2\) wave functions can overlap and thereby reduce the accuracy of the calculated adsorption energies.

| Table 1. Calculated and Experimental Lattice Parameters for Monoclinic ZrO\(_2\) |
|----------------|-------------------|------------------|
| m-ZrO\(_2\) | vdB-DFT | exp\( ^{22}\) |
| volume (nm\(^3\)) | 0.1422 | 0.1409 |
| a (pm) | 516.6 | 515.1 |
| b (pm) | 521.5 | 521.2 |
| c (pm) | 535.5 | 531.7 |
| β (deg) | 99.67 | 99.23 |

DOI: 10.1021/acs.jpcc.6b03861
theless, the trends when comparing different metal adsorbates or different oxide structures should not be affected too much.

For modeling the ultrathin ZrO₂ films, a large model cell consisting of a ZrO₂(111) trilayer on top of a pure Pt(111) substrate was used. The experiments by Antlanger et al.⁹ have shown that the ZrO₂ layer is commensurate to a \((\sqrt{19} \times \sqrt{19})R23.4°\) superstructure with respect to the Pt lattice at the interface, which results in an oxide in-plane lattice constant of 350 pm. Meinel et al.⁸ have shown the viability of a similar configuration of a ZrO₂ thin film adsorbed on a pure Pt(111) substrate, and we have used this model cell for the current work. Modeling the Pt₃Zr alloy below the interface would require a unit cell twice as large in \(x\) and \(y\). Thus, our slab consists of a five-layer Pt(111) slab with 95 platinum atoms (bottom three layers fixed) and a trilayer of 12 ZrO₂ formula units on top. The lattice constant of the model cell is 1210.7 pm, corresponding to a Pt–Pt distance of 277.8 pm. Due to the large size of the model cell a single \(\Gamma\)-centered \(k\)-point is sufficient.

The interaction of a metal adatom and the ZrO₂ surface was studied in two steps. As a first step, the single adatom was placed above the different Zr atoms of the monoclinic m-ZrO₂(111) bulk surface and allowed to relax only vertically. After reaching such a constrained energy minimum, in-plane relaxation was also enabled to obtain a local energy minimum. For ZrO₂/Pt(111) the same procedure was used, starting on a regular \(6 \times 6\) grid (36 initial adsorption sites). For Ag and Au a second, shifted \(6 \times 6\) grid was added, resulting in 72 initial sites.

The adsorption energies are based on the difference between the energy of the combined structure and the sum of the energies of the bare slab and the free atom; the sign was chosen such that higher (positive) numbers indicate stronger adsorption. The potential-energy landscapes are obtained by interpolation of the adsorption energies, using the 72 initial (constrained) sites as well as the local minima.

3. EXPERIMENTAL RESULTS

3.1. Substrate: ZrO₂ on Pt₃Zr and Pd₃Zr(0001).

Antlanger et al.⁹ reported growth of ultrathin ZrO₂ films by oxidation of Pt₃Zr(0001). As mentioned above, upon ZrO₂ formation the uppermost substrate layers below the oxide films become enriched in Pt, which is reconstructed by contracting laterally and forming dislocation lines. In a few experiments, we prepared ultrathin ZrO₂ films different from those described in ref 9, i.e., by annealing at slightly higher temperature (≈950 °C instead of 850–900 °C). In these preparations, we find no reconstruction of the substrate underneath the ultrathin oxide. In addition, we usually find some oxide-free (metallic) areas, probably because the oxide constituents dissolve into the bulk. The oxide films on the unreconstructed substrate, in the

![Figure 3](https://example.com/figure3)

Figure 3. (a) Side view and (b) top view of a monoclinic m-ZrO₂(111) surface, with the unit cell marked in (b) and O/Zr atoms in red/green. The numbers are the heights of the atoms in the first trilayer (values in picometers (pm), with respect to the average Zr height). The asterisks mark the highest 2-fold coordinated O atoms.

![Figure 4](https://example.com/figure4)

Figure 4. STM images of Ag on ZrO₂ films on (a–f) Pt₃Zr and (g, h) Pd₃Zr. (a, b) 0.26 ML deposited at RT on ZrO₂/Pt₃Zr; clusters at steps (cyan dashed–dotted lines) and oxide domain boundaries (yellow broken lines) are marked in (b). (c) Topmost terraces of clusters at terraces and steps, shown with inverted gray scale. (d) Cluster height distribution; the contributions from different nucleation sites are indicated by different colors. Panels e and f show a higher coverage (5.6 ML) of Ag on ZrO₂/Pt₃Zr as deposited at RT, and postannealed to 200 °C, respectively. (g) 0.15 ML Ag on ZrO₂/Pd₃Zr deposited at RT, with the corresponding cluster height distribution in (h).
Table 2. Densities, Predominant Apparent Heights of the Clusters, and Average Number of Atoms per Cluster for Submonolayer Coverages of Different Metals Deposited on Various Trilayer ZrO2 Substrates at Room Temperature*

<table>
<thead>
<tr>
<th>substrate</th>
<th>ZrO2/Pt3Zr</th>
<th>ZrO2/Pt3Zrunrec</th>
<th>ZrO2/Pd3Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>cluster material</td>
<td>Ag</td>
<td>Au</td>
<td>Pd</td>
</tr>
<tr>
<td>coverage (ML)</td>
<td>0.26</td>
<td>0.10</td>
<td>0.14</td>
</tr>
<tr>
<td>cluster density (10¹⁶ m⁻²)</td>
<td>0.53</td>
<td>2.3</td>
<td>3.0</td>
</tr>
<tr>
<td>predominant height (nm)</td>
<td>1.4</td>
<td>0.43</td>
<td>0.45</td>
</tr>
<tr>
<td>average number of atoms/cluster</td>
<td>464</td>
<td>41</td>
<td>45</td>
</tr>
</tbody>
</table>

*Apparent heights of single atoms or few-atom clusters depend on various factors like the sharpness of the tip; in this case a typical value of 0.1 nm is given.

Figure 5. Removal of two Ag clusters on ZrO2/Pt3Zr by the STM tip (a–c). The previous cluster positions are indicated by the broken yellow lines in the top-view image at the right. The clusters had nucleated above nodes of the substrate reconstruction.

following named Pt3Zrunrec, differ from those obtained via the standard preparation where the substrate is reconstructed. Currently it is uncertain what causes the difference between the oxide on the reconstructed and unreconstructed substrate. One possibility is a slight reduction of the oxide (some O diffusing into the substrate, leaving ZrO2-δ behind, with vacancies in the lower oxygen layer). This would lead to stronger ZrO-δ-Pt bonds and thereby lift the Pt reconstruction.

Apart from the special case of ZrO2 on the Pt3Zrunrec surface, which leads to a much higher cluster density compared to ZrO2 on the “normal” reconstructed Pt3Zr substrate (see below), the oxide films used in the present work are the same as those described in ref 9 for Pt3Zr and ref 10 for Pd3Zr. The preparation parameters were chosen such that 3D oxide clusters as described in ref 11 were virtually absent.

3.2. Ag Clusters. Figure 4a,b shows STM images of 0.26 ML (with respect to the 0.35 nm ZrO2 lattice) of Ag on ZrO2/Pt3Zr deposited at room temperature (RT). The apparent height of the clusters is mostly between 0.8 and 2.5 nm. Apart from a few clusters at regular terrace sites, a high density of clusters is found at steps [marked by cyan dashed–dotted lines in Figure 4b] and at domain boundaries of the oxide (broken yellow lines). The domain boundaries separate the two different rotation angles of the oxide on the substrate (±6.6°, ref 9). We have verified their presence by taking the Fourier transforms of the STM image on both sides of the domain boundary; the moire pattern of the domains is rotated differently (not shown). It should be noted that clusters do not decorate the steps everywhere [white arrow in Figure 4b], probably because the oxide can cover steps like a carpet; Ag does not nucleate if the oxide lattice is only slightly distorted there. The cluster density strongly depends on the step density; the value in Table 2 is for areas with few steps as in Figure 4a.

When increasing the image contrast for each cluster, so that only its topmost 250 pm is shown, we find that most clusters at terraces and also many clusters at steps show a rounded, triangular shape of the uppermost monolayer; see Figure 4c. This indicates clusters oriented with the Ag(111) plane parallel to the surface. Confirmation of this cluster orientation comes from the analysis of the apparent heights of the clusters [Figure 4d]; it shows sharp peaks with a separation of 0.24 nm, in good agreement with the Ag(111) interlayer distance of 0.236 nm. The assignment of the apparent heights to the number of Ag monolayers shown at the top of Figure 4d is explained in section 2.2. The peaks are present in the distributions for clusters at terraces (dark blue) and steps (cyan). Even the few clusters at domain boundaries (yellow) show a peak at 5 ML Ag(111). Clusters at terraces are typically taller than those at steps and domain boundaries (predominant height 7 vs 5 ML), which can be explained taking into account that clusters can collect material from a larger area if they are more widely separated.

Concerning the clusters at the terraces, we could determine their nucleation sites by removing them with the STM tip. When scanning with the tip very close to the surface (~2 mV, 0.3 nA), the tip can pick up a cluster and remove it, as shown in Figure 5. Due to the convolution with the tip shape, the clusters appear wider than they are, so we take the position of the top of a cluster as an indication for its position, not the much larger area of the base as it appears in STM images. The cluster positions are marked in the STM image at the right of Figure 5. The bright lines appearing ~1 nm wide in the image are substrate dislocations; we find that the nucleation sites of the clusters are above nodes of the dislocation pattern. At these positions, the misfit dislocations intersect the Pt surface, resulting in a large distortion of the metal, which probably also distorts the oxide above. We see no clear indication for a defect in the oxide at these positions (the bright dots seen at the position of the left cluster have been at least partly created by scanning after removal of the cluster). Easy removal of Ag clusters with no remainder indicates weak bonding of the clusters to the oxide.

The clusters are stable upon annealing to 200 °C; their density and height distribution remain unchanged within the experimental accuracy. When annealed further, above 400 °C (not shown), most Ag clusters disappear; presumably by diffusion underneath the oxide. Possibly, Ag gets dissolved into the Pt3Zr bulk.

Figure 4e shows a higher Ag coverage, 5.6 ML of Ag on ZrO2/Pt3Zr deposited at RT, and Figure 4f, postannealed to 200 °C. Already after deposition, many clusters show larger flat terraces at the top (up to ~10 nm wide); again we often
observe truncated triangular or hexagonal shapes indicative of a (111) orientation. Typical cluster heights are 3–6 nm. After annealing to 200 °C, we observe coalescence of clusters, mainly at steps [stripe-like features in the upper half of Figure 4f]. Images of the large terraces indicate a superstructure with \( \approx 0.57 \) nm periodicity, as shown by the Fourier transform in the inset. This is close to the 0.56 nm periodicity of the Pt\(_{3}\)Zr substrate, and it is also unrotated with respect to the Pt\(_{3}\)Zr lattice. Nevertheless, it is unlikely that the metal substrate periodicity should modulate the surface of a 2 nm thick island, especially when considering that a pure Pt layer (at the top of the substrate) and the oxide is in between. Within the experimental accuracy, the periodicity might also correspond to a (2 \times 2) superstructure with respect to Ag(111). Anyhow, the origin of this superstructure is unknown.

We have calculated the contact angles of the Ag clusters on ZrO\(_2\)/Pt\(_{3}\)Zr(0001) from the corrected cluster heights, as described in section 2.2 and ref 15. For a coverage of 0.26 ML we obtain a value of \( \alpha = 85 \pm 10^\circ \) (2\( \sigma \) error bars); additional experiments with annealing to 200 °C or deposition at 100 °C instead of RT did not cause any significant change of either the appearance of the images or the calculated contact angle. Also, deposition of 5.6 ML at RT leads to the same contact angle within the error bars. This indicates that the contact angle is determined by equilibrium thermodynamics, not limited by diffusion kinetics. We can therefore calculate the work of adhesion from the contact angle using the Young–Dupré equation.\(^{15}\) With \( \alpha = 85^\circ \), the work of adhesion is 1.33 J/m\(^2\) (assuming a surface energy of \( \gamma_{Ag} = 1.24 \) J/m\(^2\), ref 26). Figure 4g shows 0.15 ML of Ag deposited on ZrO\(_2\) at the other substrate, Pt\(_{3}\)Zr(0001), again at RT. In spite of a slightly lower Ag coverage than in Figure 4a, the nucleation density is about 10 times higher, which results in a much lower number of atoms per cluster (cf. Table 2). Therefore, the clusters are much smaller and appear lower; the largest peak in the cluster height distribution is at \( \approx 0.7 \) nm [Figure 4h and row “predominant apparent height” in Table 2]. According to Figure 2b this corresponds to two Ag(111) monolayers. There is also a weak peak at 3 ML height. The smaller clusters show a continuum of heights with only a weak indication of a peak at single-monolayer height (slightly below 0.5 nm), probably because their lateral extension is too small for an accurate determination of their height. In addition, the oxide buckling\(^{10}\) will lead to different geometric heights and further smear out the distribution. The number of clusters with low apparent height (<0.1 nm) is uncertain as local maxima of the substrate corrugation also contribute to the distribution; in other words, very small clusters or single Ag atoms (if any) cannot be easily discriminated against the background.

Due to the inaccurate cluster heights, we cannot calculate an exact value of the contact angle for Ag/ZrO\(_2\)/Pt\(_{3}\)Zr(0001); nevertheless, even a rough estimate shows that it must be much smaller than for the oxide on the Pt\(_{3}\)Zr(0001) substrate, and the work of adhesion is much higher (about a factor of 2).

3.3. Au Clusters. Figure 6 shows STM images of 0.1 ML of Au deposited at RT on ZrO\(_2\)/Pt\(_{3}\)Zr with (Figure 6a) and without (Figure 6b) dislocations, as well as 0.06 ML of Au on ZrO\(_2\)/Pt\(_{3}\)Zr (Figure 6c). On regular terraces of the “usual” (i.e., sublayer-reconstructed) ZrO\(_2\)/Pt\(_{3}\)Zr substrate [Figure 6a], Au forms flat islands with lateral extensions of typically 3–5 nm. Based on the rounded, hexagonal shape of some islands, we assume a close-packed Au layer equivalent to Au(111). With the exception of small clusters, which are blurred by the finite resolution of the STM image, and clusters at oxide domain boundaries or steps, almost all Au islands exhibit a two-dimensional (2D) shape with an apparent height of about 0.40 nm; some protrusions on these islands appear \( \approx 50 \) pm higher than the surrounding (line scan in the inset, Figure 6a). As we determine the apparent height distribution (bottom inset) using the highest point of each island, these protrusions also shift the maximum of the distribution to \( \approx 0.45 \) nm. The nature of these protrusions is unknown; we can exclude quantum-well states (standing waves) of electrons since the pattern does not depend on the bias voltage. The total island area on the plain terraces measured in the STM images (\( \approx 9\% \) of the terrace area) is comparable to the nominal Au coverage when assuming islands consisting of an Au(111) monolayer (7\%); thus the islands at the terraces are 1 ML thick. In contrast to Ag, the Au islands do not show signs of a triangular shape related to the 3-fold symmetry when stacking close-packed planes. This also supports the notion of single-monolayer islands. The apparent Au island height of \( \approx 0.40 \) nm is less than that of Ag(111) monolayers (\( \approx 0.55 \) nm) calculated as described in section 2.2. Only a small fraction of this difference can be attributed to a lower Au–ZrO\(_2\) interlayer distance (stronger interaction, as indicated by the 2D growth): the main contribution must be due to electronic reasons. As mentioned above, for these thin islands, we expect that most of the tunneling electrons travel ballistically through the Au island and oxide into the substrate.
which means that the oxide contributes to the tunneling barrier,
reducing the tunneling probability.

At step edges (not shown) and domain boundaries of the oxide,
thicker clusters with a predominant apparent height of
≈0.75 nm are found [see the small peak in the height
distribution of Figure 6a]. This height can be attributed to 2
ML Au(111). The tail toward higher thickness values in the
cluster height distribution does not allow us to determine
whether the higher clusters are (111) oriented or not.

On the unreconstructed substrate ZrO2/Pt3Zrunrec [Figure
6b], the cluster density is higher than on the reconstructed
substrate (Table 2). We find many small clusters (some of
them possibly even single atoms) with an apparent height in
the 0.1−0.15 nm range. A few of the smallest protrusions, with
an apparent height of ≈0.1 nm, might be adsorbed H2O from
the residual gas, as this is the typical apparent height for that
adsorbate. Most of the larger clusters appear as 2D islands with
apparent heights around 0.4 nm; as described above, this
corresponds to a single close-packed Au monolayer. In
addition, a few thicker clusters are found at the terraces.
(The cluster height distribution in Figure 6b does not include
steps or domain boundaries of the oxide.)

On ZrO2/Pd3Zr, the Au cluster density is even higher, so the
clusters are again smaller [Figure 6c and Table 2]; extended 2D
monolayer islands are no longer formed. The island height
distribution is rather broad. This is due to the finite lateral
resolution of the STM, which reduces the apparent height with
decreasing lateral extension of the clusters. Possibly the higher

corrugation of the heavily buckled trilayer ZrO2 film also
plays a role. Nevertheless, even the largest clusters are probably
not thicker than one Au layer, as deduced from their apparent
height, which is below 0.4 nm.

3.4 Pd Clusters. Figure 7a shows 0.14 ML of Pd deposited
at RT on ZrO2/Pt3Zr. Pd clusters nucleate preferentially at
steps (not shown) and domain boundaries (between the yellow
dotted lines) of the oxide, similar to what has been observed for
Ag and Au. Apart from very small clusters with an apparent
height below 0.3 nm at domain boundaries, most clusters
appear ≈0.4 nm high or slightly higher, which we can again
attribute to a single monolayer. Further maxima in the height
distribution appear at integer multiples of the Pd(111)
interlayer distance (0.225 nm) above this
first maximum, indicating (111) orientation of the clusters. The same interlayer
distance is also found upon deposition of higher coverages,
such as 1.5 ML in Figure 7b. When annealing the surface in
Figure 7b to 100 or 200 °C, the cluster density decreases only
moderately due to sintering. A significantly lower cluster
density and larger (111) facets can be achieved by deposition at
a sample temperature of 100 °C, as shown in Figure 7c.

For 0.11 ML deposited on the other substrate, ZrO2/Pd3Zr,
only few-atom clusters (probably including single atoms) are
found at the surface, as shown in Figure 7d. Similar to Au/
ZrO2/Pd3Zr, the apparent height of the smallest species is not
large enough to clearly distinguish them from protrusions of the
highly corrugated oxide; thus the cluster densities and average

Figure 7. STM images (top) and height distributions (below) of Pd: (a) 0.14 ML deposited at RT on ZrO2/Pt3Zr, (b) 1.5 ML at RT, (c) 2.2 ML on
ZrO2/Pt3Zr deposited at 100 °C, and (d) 0.11 ML on ZrO2/Pd3Zr at RT.

Figure 8. STM images of Ni deposited on ultrathin ZrO2/Pt3Zr: (a) 0.1 ML and (b) 3 ML [corresponding to 1.5 ML with respect to the Ni(111)
lattice] on ZrO2/Pt3Zr at RT. (c) 0.1 ML of Ni on ZrO2/Pd3Zr deposited at RT.
number of atoms per cluster reported in Table 2 are not very accurate.

3.5. Ni and Fe Clusters. Figure 8a shows 0.1 ML Ni deposited on ZrO\textsubscript{2}/Pt\textsubscript{3}Zr at room temperature. There are no distinct peaks in the cluster height distribution (not shown). About 90% of the clusters appear less than 0.2 nm high, indicating few-atom clusters consisting of only one layer; the similar appearance and roughly circular outline of many of the smallest protrusions (20–25%) indicate that these could be single atoms. The average cluster size determined from the cluster density and amount of material deposited is about four atoms (Table 2).

When increasing the coverage to about 0.3 nm (3 ML with respect to the ZrO\textsubscript{2} film, corresponding to \(\approx1.5\) ML Ni(111)), we observe imperfect layer-by-layer growth; see Figure 8b. The second monolayer is mostly closed, while nuclei of the third Ni layer have already formed [white in Figure 8b]. The apparent height of these small, third-layer islands is consistent with the Ni(111) interlayer distance of 203 pm. At least in some places, the dark grooves in the almost-complete Ni layer reach down more than one monolayer, which means that the oxide support is locally still accessible.

On the other substrate, ZrO\textsubscript{2}/Pd\textsubscript{3}Zr, 0.1 ML Ni leads to a much higher density of protrusions than on ZrO\textsubscript{2}/Pt\textsubscript{3}Zr, as is obvious from a comparison of Figure 8c and Figure 8a. Also, the predominant apparent height is lower, slightly below 0.1 nm. Similar to Pd and Au on ZrO\textsubscript{2}/Pt\textsubscript{3}Zr, counting the clusters is difficult because the highest protrusions in the oxide might be mistaken for clusters (or metal adatoms). Nevertheless, it is clear that the average number of atoms per cluster is below 2 (about 1.6). Therefore, we have to conclude that many of the protrusions are actually single atoms.

Finally, we have also studied the deposition of Fe on ZrO\textsubscript{2}/Pd\textsubscript{3}Zr (Figure 9). The density of clusters is comparable to Ni (Table 2). Due to the larger coverage (0.18 vs 0.1 ML), the clusters are larger; there is a clear peak in the cluster height distribution at 0.22 nm. We attribute this peak to small, monolayer clusters; their apparent height is much less than calculated for Ag in section 2.2. Again, we attribute this partly to a lower geometric height (smaller atom size and shorter Fe–oxide bonds) and partly to tunneling effects, i.e., ballistic electrons having to traverse the oxide barrier. To some degree, the lower apparent height will be also caused by the small lateral extension of the clusters (smearing out). The tail of the cluster height distribution indicates that about 20% of all clusters are thicker than a monolayer.

4. COMPUTATIONAL RESULTS

4.1. Clean Bulk and Thin-Film ZrO\textsubscript{2} Surfaces. While a cubic c-ZrO\textsubscript{2}(111) surface has flat, hexagonal layers for both Zr and O, the monoclinic m-ZrO\textsubscript{2}(111) surface (Figure 3) is strongly corrugated with strong buckling of both the oxygen and the zirconium layers. The reduced symmetry of m-ZrO\textsubscript{2}(111) leads to a variety of possible adsorption sites. In addition, a 2-fold-coordinated O atom sticks out of the surface, while the other O atoms remain 3-fold coordinated in the terminating O layer.

Our model cell shows large corrugation also for the ultrathin oxide film, similar to the calculations in ref 8. The corrugation is higher than in the previously used small models for ZrO\textsubscript{2}/Pt\textsubscript{3}Zr(0001). The thickness of the oxide film is 277 pm (core–core from highest to lowest atom). The zirconium layer of the oxide film shows a buckling of 131 pm. The ZrO\textsubscript{2} film is also heavily distorted laterally with Zr–Zr distances ranging between 320 and 447 pm. Figure 10a shows that the thin film exhibits patches where the Zr buckles upward (mainly in the bottom-left part of the unit cell; brighter Zr atoms), separated by areas more strongly bound to the substrate via the Zr atoms (Zr–Pt bond lengths are indicated for these “lower” Zr atoms). As for m-ZrO\textsubscript{2}, 1/4 of the upper oxygen atoms are 2-fold coordinated, while the remaining ones bind to three Zr atoms.

4.2. Adsorption on m-ZrO\textsubscript{2}(111). Figure 11a shows the preferred adsorption sites for metal (Me) adatoms at the m-ZrO\textsubscript{2}(111) surface. Ag and Au adatoms show weak to moderate binding energies of 0.82 and 1.22 eV respectively, as listed in Table 3. Interestingly, in contrast to all other metals, Au does not bind to the 2-fold O atom [marked by a white asterisk in

Figure 9. (a) STM image of 0.18 ML Fe on ZrO\textsubscript{2}/Pt\textsubscript{3}Zr deposited at RT; (b) cluster height distribution deduced from (a).

Figure 10. The (\(\sqrt{19}\times\sqrt{19}\))R23.4° ZrO\textsubscript{2}/Pt(111) model cell used in the calculations. The numbers in (a) indicate the distances (in pm) of the Zr and O atoms to the Pt atoms of the substrate. Panel b shows adsorption sites for Ag atoms and the corresponding adsorption energies (in eV).
Figure 11a. The energy penalty for an Au atom adsorbed in the local minimum at the favorable Ag site is 0.31 eV, about 25% of its binding energy. Pd and Ni adsorb more strongly, both at O−O bridge positions, with E_{ads} values of 2.28 and 2.71 eV, respectively. Both the Pd and the Ni atom attach to the 2-fold-coordinated protruding O atom. The second O atom participating in the bond is different for the Pd and Ni cases, as seen in Figure 11a. Due to the distortions of m-ZrO₂, with respect to c-ZrO₂, the interatomic distances in the Zr and O layers vary considerably; the small Ni atom, which has also shorter (and stronger) Ni−O bonds, prefers a position between O atoms with smaller separation than the larger Pd. Due to its stronger interaction, the Ni atom even breaks a Zr−O bond of the previously 3-fold-coordinated O atom. The increasing adsorption energy from Ag to Ni is also reflected in the decreasing Me−O bond lengths. All metal adatoms studied also exhibit Me−Zr bond lengths that indicate bonding to at least one Zr atom [Figure 11a].

A better understanding of the behavior of the metallic adsorbates is gained by inspecting the projected densities of state (PDOS) of the interacting atoms and the Bader charges of the adsorbates. The charge values given here are differences between the adsorbed and isolated neutral atom. The PDOS of the adatoms depicted in Figure 11a show two different cases: Au and Ag have their d states at low energies, overlapping with the valence band (VB) of the oxide, which is dominated by O 2p states. For Pd and Ni the d states split into a broad feature within the VB and a free-atom-like, crystal-field-split manifold in the ZrO₂ gap. Furthermore, no spin polarization is found for the Pd and Ni states, in contrast to Ag and Au where the free-atom-like, singly occupied 5s (6s) state in the ZrO₂ gap induces a small magnetic moment. As a consequence, the electronic configurations, d^{10}s^{1} in the case of

### Table 3. Calculated Adsorption Energies (eV) of a Single Metal Atom at Its Most Stable Site on the Corresponding ZrO₂ Surface

<table>
<thead>
<tr>
<th></th>
<th>Ag</th>
<th>Au</th>
<th>Pd</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-ZrO₂(1̅11)</td>
<td>0.82</td>
<td>2.14</td>
<td>2.28</td>
<td>2.71</td>
</tr>
<tr>
<td>ZrO₂/Pt(111)</td>
<td>1.82</td>
<td>2.14</td>
<td>2.71</td>
<td>3.72</td>
</tr>
</tbody>
</table>

The energy gain when moving an atom from the adatom position on ZrO₂ into the metal bulk is given in parentheses.

Figure 11. Geometry and projected electronic densities of state (PDOS) for metal adsorbates on (a) m-ZrO₂(1̅11) and (b) ultrathin (√19 × √19)R23.4° ZrO₂/Pt(111). The bond length is indicated by the thickness of the sticks: shorter bonds are shown thicker than long ones, with a cutoff at 280 and 300 pm for Me−O and Me−Me, respectively (Me = Zr or adatom). For selected bonds, bond lengths in pm are indicated. White asterisks in (a) mark the same position of the m-ZrO₂(1̅11) unit cell (2-fold O atom); see Figure 3. The number in the upper left-hand corner in the PDOS plots is the Bader charge of the adsorbate atom with respect to the isolated neutral Me atom. The PDOS for Zr and O comprise an average over the atoms nearest the adsorbate.

The Journal of Physical Chemistry C

DOI: 10.1021/acs.jpcc.6b03061

Ag and Au and d^{10} for Pd, are similar to the free atoms. The Ni PDOS is similar to Pd, which implies that an internal s–d transfer has taken place, from d^{8}s to a configuration close to d^{10}. For Ag the interaction with O is clearly visible in a broadening of the Ag 4d states, but the energy gain is not large considering the filled 4d shell of an Ag atom. The Bader charge on Ag indicates an essentially neutral atom, in agreement with the free-atom-like PDOS. Moving to Au, one finds a similar situation for the 5d states, but with an increased width of its d band, stretching down to the bottom of the VB. Furthermore, the Au 6s states interact with the O 2p states, with both effects contributing to a higher adsorption energy compared to Ag. A small charge transfer from the neighboring Zr makes Au slightly negatively charged. When comparing Pd and Ni, the stronger bonding of Ni is reflected in a stronger interaction of its d states with both O and Zr (higher O and Zr peaks at the Ni 3d energies) as well as the larger Bader charge of Ni, which is related to stronger charge transfer to oxygen.

4.3. Adsorption on Ultrathin ZrO2 Films. In addition to the adsorption energies of metal adatoms at the (111) surface of bulk m-ZrO2 discussed above, Table 3 shows the respective values at the supported ZrO2 trilayer film. One finds a large increase by 1 eV for both Ag and Ni, while Au and Pd only gain 0.5–0.6 eV. This can be understood when studying the adsorption sites: Ag and Ni, which show the largest increase of $E_{\text{ads}}$ gain one oxygen neighbor, while keeping similar Me–O bond lengths. Pd has two O neighbors on both surfaces, just that the Pd–O bond lengths are shorter on the supported ultrathin film, compared to the m-ZrO2 surface. For Ag and Pd, the adatom–Zr bonds are also shorter than on m-ZrO2. Again, gold is a special case: On the ultrathin film it has a longer (and thus weaker) bond to oxygen than on m-ZrO2. This is compensated for by a strong additional Au–Zr bond (note that its bond length of 284 pm is shorter than that of Au–Zr bonds in the Au₃Zr alloy, 298 pm).

Compared to adsorption on m-ZrO2, the PDOS plots show a broadening of the d states and a stronger interaction with the VB oxygen states for Ag, Pd, and Ni. Ni also induces Zr and O states in the band gap, again indicating strong interaction. The Ni d states are now spin-split. The minority d states are only partially filled, resulting in a magnetic moment. Also, the Bader charge shows that Ni has become a positive ion. The only atom that remains neutral on the ultrathin film is Pd. Apart from shorter bonds to both O and Zr, its bonding geometry is essentially the same on m-ZrO2 and the trilayer film, and the energy difference between the two surfaces is the lowest for all of the adsorbates studied here.

Both Ag and Au lose their free-atom-like splitting of the s states, but for very different reasons: The Ag 5s state is emptied, and also the Bader charge is indicative of an Ag$^+$ ion. For Au, the 6s state is completely below the Fermi level, and also the Bader charge indicates an Au$^-$ ion. The observation of Au$^-$ is in line with the weak (long) Au–O and strong Au–Zr bonds. The decreased interaction with oxygen is also reflected by narrowing of the Au d band. The formation of an Au$^-$ion is not universal for all adsorption sites on the ultrathin film: e.g. at the second-best adsorption site, Au resides in an O–O bridge site similar to Ag, with a Bader charge of +0.31, suggesting an Au$^+$ ion. Au$^+$ and Au$^-$ sites are also found among the other local energy minima. This finding is reminiscent of Au on CeO2(111) surfaces, where Au$^+$ can be found if an electron is available from oxidation of Ce$^{3+}$, but neutral or positive Au on the stoichiometric surface. In contrast to CeO₂, ZrO₂ is a nonreducible oxide, so the metal adatoms on the bulk oxide remain essentially neutral. Charge transfer can only occur from or to the substrate below. With Zr$^{4+}$ being the only relevant charge state, our result for ZrO₂ should be more robust than the case of Au/ CeO₂, where the details of the calculation can determine the resulting charge state.

Considering the similar adsorption energies of Ag and Au on the ultrathin film (Table 3), it is surprising that the island density of Au is much higher than that of Ag [Table 2; also compare Figures 4a,b and 6a]. Usually, this would indicate stronger interaction of Au with the oxide. We have therefore calculated the adsorption energies at a large number of sites. By interpolating between these positions, we obtain an indication of the potential-energy landscape that will be encountered by a diffusing adatom (Figure 12). The landscapes for Ag and Au are remarkably different. For Au the potential is rather flat except for a narrow and deep well, about 0.9 eV below the flat regions. Even if the barrier for diffusion between different adsorption sites is somewhat smaller than displayed in Figure 12, at room temperature, an Au adatom will remain in the potential well for a long time and diffusion will be very slow. For an Ag atom, the landscape shows many local minima with similar adsorption energies (see also Figure 10). The separating potential barriers, at least in one direction, are only around 0.45 eV. This suggests that the higher mobility of the Ag atoms as compared to Au is related to the shape of the potential-energy landscape.

5. DISCUSSION

5.1. Trends for Different Metals. In the case of low cluster densities, nucleation of metal clusters on the ultrathin zirconia films was found to be mainly heterogeneous nucleation at steps or defects. This was observed mainly for Ag and to some degree for Pd. Comparable cluster densities of Ag were also observed on the structurally similar CeO2(111) surfaces; at that surface heterogeneous nucleation is attributed to oxygen vacancies. High cluster densities (clusters at regular terrace sites) can be obtained by homogeneous nucleation only. For homogeneous nucleation, at a given substrate temperature, the density of nuclei mainly depends on the diffusion barrier for adatoms at a surface, i.e., on the corrugation of the potential-energy surface. (Transient mobility due to the adsorption energy is irrelevant at low cluster densities. The second important property is the strength of adatom–adatom bonds, which determines whether a nucleus will be stable or decay. The diffusion barrier is related to the adatom–oxide interaction, which is usually considered to increase with increasing reactivity (decreasing electronegativity) of the metal adatom. The calculated adsorption energies (Table 3)
confirm this trend with the exception of Au, which binds to the oxide more strongly than Ag. Also, when comparing experimental nucleation densities (Table 2) and calculated interaction strengths, the sequence Ag < Pd < Ni nicely shows this trend, but the experimental cluster densities for Au are more comparable to Pd than to Ag, while the adsorption energies of Ag and Au would suggest similar behavior of the two noble metals. The cohesive energies (2.95, 3.8, and 3.9 eV for Ag, Au, and Pd) might explain a higher stability of Au nuclei as compared to Ag, but cannot explain why the density of nuclei of Au is about as high as for Pd, in spite of much stronger binding of Pd to the oxide.

A further quantity to consider is the energy difference between metal adatoms and bulk metal, i.e., the energy gain when moving an adatom into a large 3D cluster (values in parentheses in Table 3). These values do not correlate with the propensity to form 3D clusters, however. For Ag, which forms large clusters and no adatoms, the energy gain is rather low. This indicates that kinetics, not energetics, is decisive for cluster growth. Coming back to adatom diffusion and nucleation, Figure 12 shows that the potential-energy surface of Au is peculiar, with a deep minimum in one site where it can bind exceptionally well to the Zr. There is a further effect that may reduce the diffusivity of Au: At the lowest-energy site, Au is a negative ion, but at other sites, where it binds to oxygen, it has to become positive. Thus, an Au adatom will have to transfer two electrons to the metal substrate for diffusion, especially when considering that the intermediate Au
d state is only weakly bound and thus unfavorable. Thus, the effective diffusion barrier is higher for Au than for Ag, explaining the higher density of nuclei for Au.

While nucleation is determined by the interaction of single atoms or very tiny clusters with the oxide, the contact angle gives an indication for the interaction of larger islands with the surface, at least if the island shape is close to thermodynamic equilibrium. For metals on TiO2, it has been shown that wetting of the oxide substrate usually increases with increasing reactivity of the deposited metal toward oxygen. The metals studied here follow this rule, with the exception of Au, which forms monolayer islands on plain ZrO2 terraces, indicative of a stronger interaction with the oxide compared to Ag and Pd. As for Au adatoms, we attribute this to strong Au−Zr bonds, while the other metals tend to bind mainly to the oxygen anions (this is similar to the Pt−Zr bonds dominating the oxide−substrate interaction on the Pt-terminated Pt3Zr9). A higher density of nuclei and more 2D-like growth of Au compared to Ag has been observed also at ultrathin alumina films on NiAl(110). As the Al cations of this film are similarly close to the surface as in the ZrO2 films, we suggest that also there a strong oxide−Au interaction has its root in bonds between Au and the cation in the oxide. All the experimental data indicate that, among the metals studied here, Ag shows the weakest interaction with the oxide (note the possibility to pick up Ag clusters with the tip, Figure 5). Three-dimensional growth has been also found for Ag on thicker ZrO2(111) films, as well as for Cu on YSZ(111), indicating weak metal−ZrO2 interaction also in these cases. For Ni, where our STM data show almost layer-by-layer growth, high-temperature annealing at 1350 or 1500 °C in H2 atmosphere leads to dewetting. Unfortunately, our system is not stable enough for annealing at sufficiently high temperatures to ensure thermodynamic equilibrium and determine whether dewetting would also occur for Ni/ZrO2 in UHV.

5.2. Zirconia-Related Aspects. The results obtained for the ultrathin films are representative for thicker (bulk) ZrO2 with some restrictions. The main restriction is the possibility of charge transfer between adatoms and the metal support, which allows for ionization of the adatoms and thus stronger bonding. The metals under consideration are not electro-positive enough to reduce the Zr ions of ZrO2; thus the adatoms remain essentially neutral on the bulk material. The distortions of the ultrathin ZrO2 films strongly increase the nucleation, as seen by comparing the data for ZrO2/Pt3Zr and the more strongly distorted ZrO2/Pd3Zr (Table 2). This provides the interesting opportunity to tune the cluster sizes via the structure of the support. A similar trend is expected when comparing cubic and monoclinic ZrO2; indeed the calculated adsorption energies for Au and Ag on monoclinic ZrO2 are ≈0.4 eV higher compared to the results of ref 24 for cubic ZrO2(111). (In contrast to ref 24, the present calculations include van der Waals interactions, which result in somewhat higher adsorption energies. Nevertheless, the main reason for the different values must be stronger bonding at the more distorted m-ZrO2(111) surface.) With increasing distortion, the ZrO2 surfaces provide a larger variety of different adsorption sites. In addition, at the more distorted surfaces the unit cell size and, thus, the distance between the best adsorption sites tend to be larger, which also favors the occurrence of single adatoms or very small clusters, leading to a high density of nuclei. Some similarity between the ultrathin films and the surfaces of bulk-like ZrO2 is also suggested by comparison with data from the literature: The Ag cluster density on 3 nm ZrO2(111) films was estimated as 2 × 1016 m−2 (ref 44), which is between our experimental values found for ZrO2/Pt3Zr and ZrO2/Pd3Zr. For Au, rather flat 2 nm Au clusters were observed on ZrO2 particles by TEM, indicating a similar growth mode as observed by us on the ultrathin films.

Compared to other oxygen-terminated oxides, the nucleation density of metals on the ZrO2 films is exceptionally high, e.g. Pd nucleates almost exclusively at domain boundaries and steps of the ultrathin alumina film on NiAl(110), while many nuclei form at the regular terraces of the ZrO2 films. On ultrathin FeO films, to reach a Pd density somewhere in between that on ZrO2/Pt3Zr and ZrO2/Pd3Zr, the deposition temperature has to be decreased to 130 K. The reason becomes clear when studying the bonding geometries: For the late transition metals, bonding to two atoms at opposite sides is favorable. Assuming typical Me−O bond lengths around 0.2 nm, an O−Me−O geometry requires O−O distances of ≈0.4 nm with space in between for the Me atom. This is possible at open surfaces like the distorted ZrO2(111) variants (Figure 11), but not on most other oxides with in-plane O−O distances typically around 0.30 nm or less. For Au, accessibility of the metal cation is important; again this is more difficult on oxygen-terminated surfaces with typical (smaller) O−O distances and the metal cations well below the surface oxygen. In addition, the large O−O distances go hand in hand with the considerable structural flexibility of the distorted ZrO2 structures, which also allows for stronger bonding to adsorbed species.

6. CONCLUSIONS
We have studied nucleation and the initial stages of growth of metals on ultrathin ZrO2 films. With the exception of Au, the
density of nuclei, which is related to the oxide–adatom interaction, increases with increasing reactivity (decreasing electronegativity) of the metal and increasing distortion of the oxide. A similar trend is found for the growth mode: Ag shows weak wetting of the ZrO$_2$ surface, i.e., pronounced Volmer–Weber growth with a contact angle of about 85°. With increasing reactivity of the metal, the growth mode changes gradually toward 2D growth. DFT calculations agree with these trends and also show why Au is an exception: Au can strongly bond to Zr and even become a negative ion, while the other metals are charge-neutral or positive and mainly bind to oxygen. We argue that many trends obtained for metals on the ultrathin zirconia films should be also applicable to metals grown on the surfaces of ZrO$_2$ nanoparticles or bulk material. The large O–O distances of ZrO$_2$(111)-like surfaces and the distortions with respect to the cubic phase provide for favorable bonding geometries not present on many other oxygen-terminated oxides.

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: schmid@iap.tuwien.ac.at. Tel.: +43 1 58801 13401.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The work was supported by the Austrian Science Fund under Project No. F45 (Functional Oxide Surfaces and Interfaces, FOXSI) and the COST Action CM1104 of the European Union. U.D. acknowledges support by the ERC Advanced Grant “OxideSurfaces”. The Vienna Scientific Cluster (VSC) is gratefully acknowledged for the generous supply of CPU time.

**REFERENCES**


