1. Introduction

The various forms of zirconia (ZrO₂) find applications in engineering and dentistry [1], catalysis [2], gas sensors [3] and solid oxide fuel cells [4, 5] because of their favorable properties, such as high mechanical strength, high melting point (2983 K), electrical insulation due to a large electronic band gap (≥5 eV) [6, 7], and oxygen ion conductance in doped form (with O vacancies). Pure ZrO₂ undergoes phase transformations from monoclinic (Baddeleyite, at room temperature) to tetragonal (above ≈1478 K at ambient pressure) and then to the cubic calcium fluorite structure (above ≈2650 K) [8–10].

The insulating nature of ZrO₂ has been a major obstacle to studying its surface as most surface science techniques such as STM require a conducting sample. To overcome this problem, previously ultra-thin zirconia films have been prepared by vapor deposition of Zr on a Pt(1 1 1) substrate in an oxygen atmosphere (typically 10⁻⁶ mbar), followed by post-annealing.
This resulted in a cubic zirconia structure with (1 1 1) termination [11–14], in agreement with DFT calculations showing that the (1 1 1) surface has the lowest surface energy [15]. This preparation method of zirconia was successful, but evaporation of Zr is difficult due to its high melting point and low vapor pressure at the melting temperature. Recently, an alternative method of preparing ultra-thin zirconia films was proposed: the oxidation of a zirconium alloy [16].

In previous work, ultra-thin zirconia trilayer (O-Zr-O) films were grown by oxidation of a Pt3Zr(0 0 0 1) alloy, and atomic resolution was achieved by STM [16]. On that substrate, growth of ZrO2 is self-limiting: O2 dissociates on the oxygen-terminated surface and thus cannot adsorb. A metal surface would be required for O2 dissociation, cf. the alumina film on NiAl(1 1 0) [17, 18]). Thus, once formed, the oxide film prevents further oxidation of the surface. The in-plane lattice parameter of the ZrO2 trilayer on Pt3Zr(0 0 0 1) was determined as 350 ± 2 pm [16]. As Zr is consumed for oxide growth, a Pt-rich substrate is left behind. At least the uppermost substrate layer beneath the oxide consists of pure Pt, which reconstructs, similar to the Pt(1 1 1) surface reconstruction [19]. The dislocation lines of the reconstruction beneath the oxide cause height variations and, hence, inhomogeneity of the ZrO2 film on Pt3Zr(0 0 0 1). In addition, small metal islands appear under the ultra-thin oxide film, which were also attributed to the Pt reconstruction [16]. Thus, the dislocations cause considerable complexity. In addition, Pt3Zr single crystals are difficult and expensive to grow. This motivated ZrO2 growth on Pd3Zr(0 0 0 1) as an alternative substrate. Both Pt3Zr and Pd3Zr fulfill the criteria for successful growth of ultra-thin oxide films: high thermal stability combined with chemical order, which impedes easy bulk diffusion of the reactive metal, resulting in slow oxidation. The latter property is especially important for growing well-ordered films. For both substrates, the affinity of oxygen to Zr is much higher than to the less reactive metal (Pt or Pd).

In many aspects, Pd3Zr(0 0 0 1) is very similar to Pt3Zr(0 0 0 1), having the same bulk structure (Ni3Ti-type, D024; figure 1) and similar lattice parameters. Pd3Zr(0 0 0 1) and Pt3Zr(0 0 0 1) are isostructural, and both are so-called Engel–Brewer alloys [20, 21], which explains the high thermal and chemical stability of these ordered alloys. However, because Pd3Zr crystals are easier to grow (lower mass density and lower melting point), they are less expensive compared to Pt3Zr.

In this paper we report on the growth of zirconia trilayer O-Zr-O films by the oxidation of Pd3Zr(000 1). The surface was studied with STM, AES and XPS. The experimental work is supplemented by DFT studies. The zirconia films on Pd3Zr(000 1) are similar to ZrO2/Pt3Zr(000 1). A number of significant differences are caused by the absence of a (reconstructed) pure-metal layer underneath the ultra-thin oxide.

2. Experimental and computational methods

2.1. Experiment

The experiments were conducted in a two-chamber ultra-high vacuum (UHV) system. The base pressure was below 10−10 mbar in both chambers. This system is equipped with components for standard sample preparation (Ar+ ion sputter gun, electron beam heater, leak valves) and surface analysis (STM, XPS and AES). The same system was used in our previous work on Pt3Zr [16]. Sample temperatures were measured by a thermocouple connected to the side of the sample holder. This leads to a systematic error at high temperatures where temperature gradients are large. The error was corrected by measuring the temperature with a disappearing-filament pyrometer. We estimate that the temperatures given are accurate within ±20 K.

The Pd3Zr(000 1) sample, bought from MaTecK (Germany), was cleaned by standard sputter-anneal cycles with 45 min of sputtering (2 keV Ar+, 3 µA cm−2) and annealing at 870 °C in UHV. AES and XPS revealed oxygen as the major impurity, present in the as-delivered crystal and also incorporated by our oxidation experiments. We found that the residual oxygen can cause a rough alloy surface after annealing. In order to reduce the O concentration in the bulk, automated overnight preparation with ≈10 cycles of sputtering at room temperature, annealing at 870 °C and cooling to room temperature was used. These cycles reduced the O concentration in the bulk. Thereafter an alloy surface with large terraces (=80 nm) could be prepared reproducibly, although roughly 1% of oxygen was always present. To prepare the ultra-thin zirconia trilayer, Pd3Zr(000 1) was first oxidized at 400 °C sample temperature by backfilling the preparation chamber with O2 at 7×10−9 mbar, and then post-annealed at 870 °C for 10 min in UHV.

The STM measurements in this work were performed at room temperature with electrochemically etched tungsten tips. For the AES measurements, a cylindrical mirror analyzer with a coaxial electron source emitting a 3 keV beam was used. We observed a decrease of the O peak in the Auger
spectra over time: the high-energy electron beam destroys the oxide on the surface, due to electron stimulated desorption of oxygen. Hence, the measurements were conducted in a manner that minimizes the exposure time to the electron beam. A single AES measurement, limited to the relevant peaks only, took $\approx 10$ s. This reduced the error to less than 1% of the peak height. XPS measurements were carried out with MgK$\alpha$ radiation (electrons: 15 kV, 15 mA emission) and a hemispherical analyzer. Peak intensities were analyzed by fitting with the FitXPS program.

2.2. Determination of lattice parameters from STM images

For accurate measurements of lattice parameters, it is important to correct the STM images for nonlinear distortion caused by creep of the piezoelectric STM scanner, as well as linear distortions due to thermal drift, non-orthogonality of the scanner and inaccurate scanner calibration. For the correction of nonlinear distortions, a suitable function is required to describe creep of a piezoelectric element. In the literature, creep is described by various functions, usually with a logarithmic dependence on time [23], though a power law [24], polynomials [25] or response of multiple viscoelastic elements [26] are also used. These functions depend on scan size and speed; furthermore their application requires that the history of the scanner voltage is known (e.g. recent translations to set the imaging position, restarts of the scan). For STM data acquisition systems this is usually not the case. Therefore, for the current work a different approach was employed, using a simple function that in our experience describes creep well enough: the tip position in the slow-scan direction is assumed as

$$y(t) = y_0 + a t + b \sqrt{t-t_0},$$

where $y_0$, $a$, $b$ and $t_0$ are constants; $t_0$ is before the recording of the image starts. In contrast to the functions mentioned above, only two parameters $b$ and $t_0$ describe the nonlinear distortion. The two other parameters $y_0$ and $a$ are adjusted such that the borders $y = 0$ and $y = y_{\text{max}}$ of the image remain the same as when assuming no distortion. Having only two free parameters makes their determination easy using an optimization procedure: when the distortions of the STM image are successfully corrected, the peaks of a regular lattice (usually substrate peaks) should reach maximum intensity in the fast Fourier-transform (FFT) of the corrected STM image. Optimization is based on the Nelder-Mead simplex algorithm, in a form very similar to that described in [27], implemented in the public-domain image-processing program ImageJ [28]. Usually, the distortions in the fast-scan direction ($x$) and shear distortions can be neglected, though for some images we need to account for these distortions. In this case (1) was also used for these distortions (with $y$ replaced $x$), and the optimization was done for all parameters simultaneously.

2.3. Computational set-up

To gain a deeper understanding of the interface between the substrate and oxide, DFT calculations were employed, using either standard DFT or DFT calculations including van-der-Waals contributions. The DFT studies were done with the Vienna Ab-initio Simulation Package, which uses a projector augmented-wave formalism to describe the interactions between atoms [30, 31]. An energy cutoff of 400 eV and fine Γ-centered k-point meshes (see below) automatically generated with the Monkhorst–Pack scheme [32] ensured electronic convergence of the calculations. To determine the optimum structures, relaxation was done until the residual forces were below 0.01 eV Å$^{-1}$. For the surface calculations, 15 Å of vacuum was placed between the periodic repetitions.

In some calculations, the generalized gradient approximation (GGA) as proposed by Perdew, Burke and Ernzerhof [33] (PBE) was used to treat the electronic exchange and correlation effects. For the most part, however, the van-der-Waals density-functional (vdW-DF) method was used to account for the van-der-Waals interaction as proposed by Dion et al [34]. The implementation used here is the so-called optB88 functional [35], which is based on a modified Becke88 DFT functional [36]. Compared to other vdW-DFs, optB88 gives more accurate results for both adsorption energies and crystallographic parameters [37].

To test the two DFT functionals used, the size of the unit cell and formation energy of bulk ZrO$_2$ were calculated and compared to experiments (table 1). For cubic ZrO$_2$, which is unstable at room temperature, experimental room-temperature lattice parameters were obtained for metastable samples, with values of 509 [38] or 513.5 pm [39]. Somewhat better data are obtained by extrapolation from doped (stable) cubic ZrO$_2$ to zero doping, yielding lattice parameters of 510–512 pm, corresponding to a volume of 0.0331–0.0336 nm$^3$ per ZrO$_2$ formula unit [40, 41]. A comparison of these values and the calculated ones, as well as the data for monoclinic ZrO$_2$ (table 1), shows that both functionals are accurate within $\leq 3\%$ for the volume (which corresponds to $\approx 1\%$ for the lattice parameters). The energies are more important, however, and here the vdW-corrected optB88 potential gives better heats of formation for ZrO$_2$ (table 1). As a vdW-corrected functional was also required to correctly describe bonding of the ultra-thin ZrO$_2$ film on Pt$_x$Zr(0001) [16], all calculations in the current paper are based on optB88 unless noted otherwise.
3. The Substrate: Pd3Zr(0 0 0 1)

3.1. Experimental observations

Concerning preparation, our AES and XPS spectra indicate only weak preferential sputtering: assuming that the annealed surface is stoichiometric as indicated by STM (see below), the near-surface layers of the sputtered surface have a Zr concentration of approx. 21% (AES) or 24% (XPS). As AES has a lower probing depth due to lower electron energies, this indicates slight Pd enrichment at the sputtered surface, but almost bulk-like concentrations below.

Preparation of the alloy by sputter/anneal cycles, with a final anneal at 870 °C, results in large terraces (>50 nm) with a step height of ≈0.45 nm (figure 2(b)). This step height is consistent with the interlayer distance between two equivalent planes of the Pd3Zr bulk structure. This suggests that the ordered phase and thus the stoichiometry of the bulk has not been destroyed by the preparation procedure. This is noteworthy as the stability range of the ordered Pd3Zr alloy is only a few percent. The step height implies that the surface termination of Pd3Zr(0001) is either always an A layer or always a B or C layer (the latter two are equivalent, see figure 1), which is in agreement with the DFT results (see below).

In the case of Pt3Zr(0001), domain boundaries of the alloy intersecting the surface were observed when the sample was heated to insufficiently high temperatures or when the stoichiometry was incorrect [16]. This was attributed to the narrow chemical stability range of the Pt3Zr(0001) alloy. These domain boundaries appeared as straight lines oriented along the close-packed directions of the crystal, often accompanied by steps with a height of c/4 = 0.23 nm. For Pd3Zr(0001), after annealing at temperatures below 800 °C, such straight lines were not observed. Nevertheless, steps with c/4 height occur on this surface, indicating different translational domains of the ordered Pd3Zr phase (figure 2(a)).

Atomic resolution STM images of Pd3Zr(0001) show a hexagonal lattice with protrusions at a periodicity of 0.56 nm (figure 3). Through comparison with the structure model (figure 1) the protrusions are readily identified as the Zr atoms. A bulk-terminated surface, i.e. essentially no surface segregation, is often found for (super-) alloys with a strong chemical order [44]. There are also a few dark defects, located either at Zr sites (labelled ‘A’ in figure 3) or between Zr atoms (B). Most likely, type A is anti-site Pd or an impurity atom replacing Zr. The dark spots between the Zr atoms (B) are attributed to oxygen.

Even without dosing additional oxygen, sometimes a zirconia trilayer film was observed on the alloy after annealing, even up to completely covering the surface. This is due to oxygen contamination and indicates that oxygen diffusing from the bulk can form ZrO2 on the surface.

3.2. DFT results

DFT calculations provide a closer insight into the properties of the Pd3Zr substrate. To determine the surface termination of the substrate, the surface energy was calculated for two different Pd3Zr(0001) five-layer slabs with A and B/C termination. The cell size was fixed at the bulk values in x and y direction, while the atoms were allowed to relax their individual positions; a 12x12x1 k-point mesh with 74 irreducible k-points was used. For the A-terminated slab, the calculated surface energy of 749 meV/atom (650 meV/atom) was lower than for the B/C termination by 57 meV (55 meV) per atom, when using the optB88 (PBE) functional. Thus, the surface termination of the clean surface is an A layer, similar to Pt3Zr [16]. The surface relaxations were also determined by vdW-DF (PBE gives similar results). Compared to the bulk, the interlayer distances show a contraction of the first and an expansion.

### Table 1. Properties of cubic and monoclinic bulk ZrO2 calculated with two different functionals and compared to experimental data.

| Structure | Cubic | Monoclinic |
|-----------|-------|------------|
| Volume (nm$^3$/ZrO$_2$) | 0.03361 | 0.03396 | 0.03638 | 0.03616 | 0.03522 a |
| Heat of formation (eV/ZrO$_2$) | 10.19 | 10.97 | 10.40 | 11.13 |
| Heat of formation (kJ mol$^{-1}$) | 983 | 1058 | 1003 | 1073 | 1092 b |

a $T = 295$ K [9]

b $T = 0$ K [42]

### Table 2. Calculated and experimental [43] lattice parameters and equilibrium volume for bulk Pd$_3$Zr.

|          | PBE   | optB88 | Expt |
|----------|-------|--------|------|
| a (pm)   | 569.9 | 569.3  | 561.2 |
| c (pm)   | 931.0 | 934.9  | 923.5 |
| Volume (nm$^3$) | 0.2619 | 0.2624 | 0.2519 |

To examine whether vdW-DF calculations also offer an appropriate description of the metallic substrate, the lattice parameters of the bulk alloy were determined with both the GGA and the vdW-DF approach (12x12x12 Γ-centered k-point grid with 301 irreducible k-points). In agreement with previously published data [35], we find that both functionals predict very similar lattice constants and slightly overestimate the lattice parameters (table 2). Compared to the experimental values, for the PBE functional a and c are too large by 1.5% and 0.8% respectively; for the vdW-DF functional the values are similar (1.4% and 1.2%). In the following, interlayer distances, bond lengths, etc. are given as calculated; no scaling to the experimental lattice parameters was applied. Adsorption energies of the oxide film on the alloy are given per ZrO$_2$ formula unit, calculated as the difference between the oxide-covered alloy and the sum of the energies of the clean alloy slab and a free-standing ZrO$_2$ trilayer film with its in-plane equilibrium lattice parameter (329.9 pm).
of the second interlayer distance, by −2.4 and +0.3%, respectively. In the surface layer the inwards relaxation is larger for Zr (−8.1%) than for Pd (−0.4%). The large inwards relaxation for Zr is surprising, considering that a Zr atom is larger by 16% than a Pd atom. The same was also found for Pt3Zr, where the size difference is similar [16]. Experimental (−2.3% [45]) and calculated (−2.8 to −6.4% [46]) values for the first interlayer contraction of pure Zr are more moderate. Thus, the large inwards relaxation of Zr is a special property of the Pt3Zr and Pd3Zr alloys. As on Pt3Zr(0 0 0 1), one reason for the unusual relaxation lies in opposite Zr relaxations of the surface and subsurface layers: in the second layer, the Pd atoms slightly buckle down (13 pm below the second-layer Zr), thus the Zr sitting above three Pd atoms (see figure 1) can relax inwards. The Pd atoms in the surface have an upwards-buckled Zr neighbor in the second layer, so they cannot buckle down as much as the Zr. Nevertheless, the Zr atom in the surface has a shorter distance (275 pm) to its 2nd-layer Pd neighbors than the first-layer Pd atoms (287 and 276 pm to subsurface Pd and Zr, respectively).

To compare the Pd3Zr(0001) surface with Pt3Zr(0001), where a Pt termination is found after oxidation [16], the equivalent configuration was also studied, i.e. a hypothetical Pd-terminated surface (surface Zr replaced by Pd). Similar to the alloy substrate, A termination is more stable than B/C, but the surface energy difference is much lower, 7 meV. The relaxations reach further down into the bulk than on the stoichiometric alloy, thus a nine-layer slab was used. The interlayer distances are \(d_{12} = 224\) pm and \(d_{23} = 232\) pm (bulk: 233 pm). It is noteworthy that the contraction of the first interlayer distance (−4.2%) is higher than for the stoichiometric alloy, where Zr is mainly responsible for the contraction. It is also higher than for Pt/Pt3Zr(0001) (−0.4% [16]). The value of \(d_{12}\) for Pd/Pd3Zr(0001) is comparable to the experimental Pd(1 1 1) interlayer distance (225 pm). The buckling in the surface Pd layer is rather small (6 pm); the Pd having no Zr neighbor below is lower. The second layer shows a sizable buckling, with the Zr atom elevated 18 pm above the surrounding Pd atoms. In the layers below, the buckling is less than 4 pm. Overall, these findings are similar to Pt/Pt3Zr(0001).

4. Ultra-thin ZrO2 films on Pd3Zr(0001)

4.1. STM results

In order to prepare a ZrO2 thin film, the clean Pd3Zr(0001) sample was annealed to 400 °C in 7×10−9 mbar O2 for 30 min. Oxidation results in ≈0.2 nm high and a few nm wide islands; these cover about 1/4 of the surface (figure 4(a)). The islands and the remaining surface have a similar appearance. The existence of islands can be explained by mass transport: removal of more than half a monolayer of Zr from the alloy to form an oxide leaves islands behind [16]. Altogether, this indicates that both levels, the top of the islands and the lower level are already covered by an ultra-thin oxide. The observation of the substrate periodicity in the STM images is either due to buckling of the

Figure 3. STM image of the sputtered and annealed Pd3Zr(0001) surface. The blue lines indicate the Zr lattice to show the location of the dark defects more clearly. Defect A is attributed to a non-Zr atom in a Zr site; defect B is attributed to oxygen.
oxide or due to the fact that it is transparent for the tunneling electrons. For the annealed oxide films, discussed below, STM also shows a similar corrugation of the substrate at positive sample voltages.

Upon annealing (600 °C for 10 min; figure 4(b)), the islands grow in size to ≈10 nm diameter. The height does not change. Some islands (but not the substrate) show a superstructure. This structure was not found after high-temperature annealing.

A closed homogeneous oxide surface is obtained after annealing at 870 °C for 10 min (figure 5(a)). After annealing above 870 °C the oxide starts to disappear and areas of the clean alloy surface begin to appear. As the oxygen–zirconium bond is very strong, the disappearance of the surface oxide above 870 °C cannot be explained by desorption of oxygen. Most likely, oxygen diffuses into the bulk.

Our experiments also showed that the surface condition of the Pd₃Zr(0 0 0 1) alloy before oxidation is the key factor that determines the quality of the oxide. High oxygen concentration in the bulk induces a large number of large oxide clusters (> 10 nm in height). Although these clusters cover only a very...
small fraction of the area, the STM tip often crashes into these clusters because they are non-conducting. With our single crystal, it was impossible to completely avoid the occurrence of such clusters.

On the well-ordered ultra-thin oxide film, atomic resolution of the oxide is possible, but only at very low bias voltages, where the tip is close to the sample. At larger biases, STM shows mainly the 0.56 nm substrate lattice or a superposition of the substrate and oxide lattices as in figure 5(a). When atomic resolution of the oxide is achieved, we find a hexagonal zirconia lattice (figure 5(b)) with a lattice parameter of $d_{\text{oxide}} = 351.2 \pm 0.4$ pm. In contrast to Pt$_3$Zr(0 0 0 1), no substrate reconstruction was observed. The oxide film shows a large buckling perpendicular to the surface. The apparent height difference between upwards and downwards buckled atoms in the STM image is up to $100$ pm; the inset in figure 5(b) shows a line profile across a few atoms in the oxide. The buckling shows no clear long-range order. Locally, bright atoms are often found at a distance of $\sqrt{7} d_{\text{oxide}}$ from each other, labeled ‘moire’ at the right side of figure 5(b). This distance is close to the real-space equivalent of the moiré vectors discussed below. The buckling of the oxide film is almost twice as much as for the ZrO$_2$/Pt$_3$Zr(0 0 0 1) system [16]: After subtraction of long-range variations (high-pass filter with a width of $\sigma = 1$ nm), the standard deviation of the apparent atom heights in figure 5(b) is $25$ pm, compared to $14$ pm for ZrO$_2$/Pt$_3$Zr(0001) (figure 4(b) of [16]).

Figure 5(c) shows the Fourier transform from an STM image similar to figure 5(a). The larger size of the input image ($500 \times 60$ nm) provides for higher reciprocal-space resolution. This FFT pattern is reproducible for many preparation cycles and different areas of the crystal. In the FFT, the reciprocal lattice of the oxide is marked with solid (red) circles and the reciprocal lattice of the Pd$_3$Zr(0001) alloy is indicated by broken (blue) circles. The innermost broken circles correspond to first-order spots of the alloy, i.e., a real-space lattice parameter of $0.5612$ nm (see figure 1). The FFT shows additional maxima. These correspond to differences between the oxide and substrate lattices and are, hence, moiré spots. Each of the three moiré vectors $\alpha$, $\beta$, and $\gamma$ in figure 5(c) is shown three times: once as a vector between the two reciprocal lattices (near the top, explaining its origin), once at the (0, 0) spot (explaining the main spots inside the first-order substrate spots), and once at the first-order spots of the alloy, explaining the moiré spots further out. Additionally, there are faint higher-order moiré spots.

The moiré spots roughly fit a $(\sqrt{43} \times \sqrt{43})R7.6^\circ$ structure with respect to the 0.5612 nm alloy cell. This periodicity is also found in real-space STM images (yellow lines in figures 5(a) and (b); note the bright atoms at most cell corners), but never extends over more than one or two cell widths. Therefore, this cell does not accurately describe the superstructure. Within the experimental accuracy, the FFT spots are accurately described by a larger $(\sqrt{217} \times \sqrt{217})R10.16^\circ$ cell (side length 8.27 nm). In real space, the STM images show no clear indication of this periodicity (dark lines figure 5(a)); only occasionally bright atoms or small dark patches show this periodicity. We also find no low-order moiré spots corresponding to this periodicity in the FFT. Due to the finite reciprocal-space accuracy (related to the finite size of sufficiently well-resolved STM images), we cannot exclude an even larger or incommensurate cell. The $(\sqrt{217} \times \sqrt{217})R10.16^\circ$ cell results in a ratio between the lattice parameters of the oxide and the alloy of $\sqrt{217}/553$. This translates into an oxide lattice parameter of 351.5 pm, very close to the value obtained from the real-space STM measurements (351.2 pm). The rotation angle between the alloy and the oxide calculated from either superstructure cell is 12.3$^\circ$. This angular mismatch, or, strictly speaking, one of the two rotational domains with $\pm12.3^\circ$ rotation of the oxide was observed for all STM measurements of ultra-thin ZrO$_2$/Pd$_3$Zr(0001). As incommensurate structures typically show significant variations of the rotation angle, this observation indicates that the structure is not fully incommensurate, even though the extremely large superstructure cell in real space is untypical for commensurate structures. In this sense, we may call it a weakly commensurate structure.

On ZrO$_2$/Pd$_3$Zr(0001) there are strong moiré spots (a) caused by the difference of the oxide reciprocal lattice and the first-order spots of the alloy (figure 5(c)). In contrast, these moiré spots are virtually non-existent for the oxide on Pt$_3$Zr [16]. There, the only strong moiré spots are caused by the difference between the oxide and the second order of the substrate spots (corresponding to $\beta$ in figure 5(c)). This means that on Pt$_3$Zr, the oxide is only modulated by the 0.28 nm lattice of the substrate, not by the chemical order, which has twice that periodicity in real space. This is in agreement with the structural model where the oxide on Pt$_3$Zr binds to a pure Pt layer with a 0.28 nm inter-atomic distance [16]. For the present Pd$_3$Zr(0001) substrate, with strong moiré spots related to the $\alpha$ vector, the oxide is strongly modulated by the 0.56 nm periodicity of the substrate, suggesting that this periodicity plays a much more important role than on Pt$_3$Zr. It will be shown below that the substrate layer below the oxide on Pd$_3$Zr is not a pure Pd layer but rather a bulk-terminated alloy as shown in figure 1. The moiré spots reflect the interaction of the oxide with the chemically different Pd and Zr atoms, arranged with a 0.56 nm periodicity. Summarizing, here we simply have ZrO$_2$/Pd$_3$Zr(0001), in contrast to ZrO$_2$/Pt$_3$Zr(0001) in [16].

4.2. Spectroscopy

The O-Zr-O trilayer is the charge-neutral building block of zirconia. From STM one cannot determine whether the oxide is a single trilayer or a thicker film. To determine the thickness of the oxide, the same method was used as for the ZrO$_2$/Pt$_3$Zr(0001) system, i.e. a comparison of the oxygen Auger signals of ZrO$_2$ and oxidized Rh(1 1 1), which forms a single, self-limited RhO$_2$ trilayer [47]. The in-plane lattice distances of ZrO$_2$/Pt$_3$Zr(0001) and RhO$_2$ are 0.351 nm and 0.302 nm respectively, so a single ZrO$_2$ layer has $\approx 74\%$ of the oxygen density in the RhO$_2$ trilayer. Thus, we expect that the oxygen signal for a single ZrO$_2$ trilayer is $74\%$ of that measured for the RhO$_2$ trilayer. The experimental O KLL peak intensity ratio between ZrO$_2$/Pd$_3$Zr(0001) and RhO$_2$/Rh(1 1 1) is $81\%$. This result fits the expectations for a single O-Zr-O trilayer.
metallic Zr, the intensity ratios of Pd3d5/2/Zr3d5/2 are 5.47 and 5.74 for sputtered and oxidized Pd3Zr(0001), respectively. A full simulation of the experimental configuration with <10% accuracy and clearly rules out a thicker oxide. A similar measurement by XPS was hampered by the overlap of the O1s and Pd3d3/2 peaks.

XPS measurements are well-suited to determine the composition of the substrate underneath the oxide. The chemical shifts in XPS provide a clear distinction between Zr in the oxide (see a forthcoming paper for details) and metallic Zr in the substrate. Taking into account only the signals of oxide (see a forthcoming paper for details) and metallic Pt layer in ZrO2/Pt/Pt3Zr), we performed simulations of the pure Pd layer at the top of the substrate (in analogy to the (329.9 pm with the optB88 functional; close to 10% compression with respect to the bulk as found in [50]). For the following discussion of the structural properties of the oxide film, we focus on the results of approach (A), but we have to keep in mind that an expanded substrate will be somewhat more reactive than the real system. With one exception (possibly related to this higher reactivity), both sets of calculations (A) and (B) give qualitatively similar results (table 3).

In the model cell, four different configurations were chosen to provide an efficient sampling of the different positions of the almost incommensurate oxide film on the substrate. These configurations can be seen as representative for the local arrangement in a small region of the large, experimental ZrO2/Pt/Pt3Zr(0001) has almost bulk composition (see section 3.1); thus also the substrate below the ultra-thin oxide has a composition close to the bulk.

For a better estimate of the influence of a (hypothetical) pure Pd layer at the top of the substrate (in analogy to the Pt layer in ZrO2/Pt/Pt3Zr), we performed simulations of the XPS intensities using the SESSA code. The simulated substrate Pd3d3/2/Zr3d5/2 intensity ratios are 5.76, 5.64 and 7.25 for clean Pd3Zr, ZrO2/Pd3Zr, and ZrO2/Pd/Pd3Zr, respectively. Thus, an additional Pd layer should be clearly detectable. XPS therefore confirms the Pd/Zr termination below the oxide. (The calculated slight decrease of the Pd/Zr intensity ratio from the substrate upon formation of an oxide overlayer is due to the lower kinetic energy of the Pd3d3/2 photoelectrons compared to Zr3d5/2; thus the Pd signal is attenuated more strongly by the oxide overlayer.)

### 4.3. DFT results

A full simulation of the experimental (√217 × √217 )R10.16° supercell is computationally very expensive. Therefore, calculations were restricted to (√3 × √3 ) models similar to those examined in [16]. We have two options for this, (A) using an in-plane lattice spacing for the oxide close to the experimental one, but expanding the substrate in x and y (allowing it to contract vertically), and (B) keeping the substrate lattice constants, which leads to an in-plane compression of the oxide lattice by 6.3% compared to the experimental value. The compressed oxide in (B) roughly coincides with the DFT equilibrium lattice parameter of an unsupported ZrO2 trilayer (329.9 pm with the optB88 functional; close to 10% compression with respect to the bulk as found in [50]). For the following discussion of the structural properties of the oxide film, we focus on the results of approach (A), but we have to keep in mind that an expanded substrate will be somewhat more reactive than the real system. With one exception (possibly related to this higher reactivity), both sets of calculations (A) and (B) give qualitatively similar results (table 3).

In the model cell, four different configurations were chosen to provide an efficient sampling of the different positions of the almost incommensurate oxide film on the substrate. These configurations can be seen as representative for the local arrangement in a small region of the large, experimental (√217 × √217 )R10.16° cell. These different configurations are called O1Pd, O1Zr, ZrPd and ZrZr, as illustrated in figure 6. For example, ‘O1Pd’ means that one of the lower oxygen atoms (O1) of the oxide is located exactly above a Pd atom of the alloy surface (broken yellow circle in figure 6(a)). To prevent relaxation into a different configuration, the lateral (x, y) coordinates of the two atoms defining the model (the O1 or Zr atom in the oxide film and the Zr or Pd atom in the surface layer directly below) were kept fixed. When this constraint is lifted, in the compressed-oxide calculations (B), the geometry of the O1Zr configuration changes into a slightly different structure (named O1Zr′), which has the largest adsorption energy of all in these calculations.

In contrast to ZrO2/Pt/Pt3Zr(0001), where the PBE functional yields very large (and unrealistic) distances between the substrate and the oxide [16], the present calculations show chemical bonding between the substrate and the oxide already with PBE: the Zr atoms in the uppermost substrate layer (S) bind to the lower oxygen (O1) in the oxide. The bonding distances hardly change when using the optB88 vdW-DF functional, but the adsorption energies for the different configurations increase. Table 3 summarizes the structural aspects of the film as obtained with the vdW-DF functional for both sets of calculations, (A) stretched substrate and (B) compressed oxide (values in parentheses).

Based on the first four configurations in figure 6 and table 3, the calculations predict an average interlayer distance of 214 pm between the substrate and the lower O layer O1. As the interlayer distance refers to the average height of the atoms in each layer, individual bonds can be shorter than this. The bond lengths already indicate the important role of Zr in the substrate for bonding: the first three configurations have at least one short bond between the Zr(S) atom in the

### Table 3. Structural parameters and adsorption energies of the model configurations and the fully relaxed O1Zr′ configuration, calculated using the vdW-DF. Values in parentheses are results for a cell with the oxide compressed by 6.3% with respect to experiment, but undistorted substrate. Interlayer distances d are between the average heights of the layers, buckling values b are peak–valley differences, and bond lengths l refer to the shortest bond between the given layers; the asterisk (*) indicates three equal bonds.

| Configuration | O1Pd | O1Zr | ZrPd | ZrZr | O1Zr′ |
|---------------|------|------|------|------|-------|
| d_{O1-Zr} (pm) | 94 (97) | 86 (96) | 85 (96) | 82 (92) | 87 (96) |
| d_{Zr-O1} (pm) | 89 (96) | 88 (97) | 90 (97) | 87 (89) | 89 (96) |
| d_{O1-S} (pm) | 220 (231) | 224 (242) | 219 (238) | 193 (211) | 226 (240) |
| b_{O1} (pm) | 79 (20) | 32 (25) | 27 (20) | 0 (0) | 30 (22) |
| b_{S} (pm) | 29 (17) | 7 (11) | 11 (11) | 27 (48) | 4 (9) |
| l_{Zr-Pd/S(min)} (pm) | 271 (283) | 306 (297) | 299 (283) | 307 (315) | 289 (289) |
| l_{O1-Zr/S(min)} (pm) | 224 (231) | 210 (221) | 209 (225) | 238 (233) | 212 (222) |
| E_{ads} (meV/ZrO2) | -568 (−412) | -563 (−480) | -545 (−454) | -405 (−459) | -566 (−508) |
substrate and an O1 atom, with bond lengths between 209 and 224 pm. All these Zr(S)–O1 bond lengths are similar to those in cubic ZrO$_2$ (223 pm with the optB88 functional). In the ZrZr configuration, the substrate Zr(S) atom binds to three O1 atoms, each at a distance of 238 pm. To keep these bonds short, the Zr(S) atom buckles outwards by 27 pm and the three O1 atoms binding to Zr(S) move closer to each other (O1–O1 distances 281 instead of 347 pm, figure 6). The bonding between O1 and Zr(S) in the substrate is the major difference between the ZrO$_2$/Pd$_3$Zr(0 0 0 1) surface oxide and its counterpart on Pt$_3$Zr(0 0 0 1). In the latter case, the substrate is terminated by a pure Pt layer, which binds very weakly to the O1 atoms in the oxide, similar to the weak Pd–O1 bonds in the present case. The shortest O1–Pd distance (O1Pd geometry) is much longer than the Pd–O bond in bulk PdO (247 versus 201 pm).

There are also bonds between Zr of the oxide and the substrate. This was already observed for ZrO$_2$/Pt/Pt$_3$Zr(0 0 0 1), where it was dominating the oxide-substrate interaction. The Zr–Pd$_{Sj}$ distance can be even shorter than the Zr–Pd distance in the bulk of Pd$_3$Zr (285 pm). Nevertheless, the O1Zr configuration has a high adsorption energy $E_{ads}$, in spite of a long Zr–Pd$_{Sj}$ bond. This clearly shows that Zr–Pd$_{Sj}$ bonds are weaker than O1–Zr(S). There are no bonds between the Zr atoms in the oxide and Zr in the substrate. This is due to the Zr(S)–O1 bonds, which push away the Zr atoms in the oxide: even in the ZrZr configuration, the Zr–Zr(S) distance is 316 pm. Here the Zr is squeezed up by the O1 triangle below it; as mentioned above this O1 triangle contracts for better bonding to the Zr(S) below.

Depending on the local configuration, our calculations predict a significant buckling of the ZrO$_2$ layer. Here, the O1Pd configuration is a special case because there the oxide is strongly distorted. This is caused by a Zr(S) atom binding to two O1 atoms (arrowed in figure 6), causing each of these O1 atoms to lose one bond to a Zr atom in the oxide. This kind of distortion is not present in our calculations with unmodified substrate and compressed oxide, thus it is uncertain as to whether it is realistic or an artifact of the expanded substrate. Apart from this special case, the O1Zr configuration and its closely related O1Zr' modification show the largest buckling of the oxygen layer at the interface (O1). The O1 atom directly above a Zr(S) is pulled closer to the substrate by 27 pm as compared to the average of the remaining two O1 atoms. However, this buckling amplitude is small compared to that of the Zr in the oxide film: depending on the local oxide/substrate configuration, the height difference between the highest and lowest Zr atom in the oxide is between 41 and 101 pm. This is partly due to Zr–Pd bonds, which pull the Zr in the oxide towards the substrate, but also related to lateral shifts of the oxygen atoms: if a Zr atom in the oxide buckles upwards, its O1 neighbors below can move closer together, and the O2 neighbors above expand their distance to make space; vice versa for Zr buckling downwards. This favors alternating upwards and downwards movements of neighboring Zr atoms. In the O1Zr configuration, this O-mediated interaction between the initially symmetry-equivalent Zr atoms prevents binding from all three Zr atoms to Pd$_{Sj}$ atoms and thereby breaks the C3 symmetry.

Although the reason for Zr buckling is the same as in ZrO$_2$/Pt/Pt$_3$Zr(0 0 0 1), the amplitudes are higher by ≈40%. For both substrates, the large buckling of the Zr layer is related to a low energetic cost of these distortions. The higher buckling amplitudes in the Pd$_3$Zr case must be attributed to the stronger interaction with the substrate (O1–Zr(S), bonds), leading to larger distortions of the film and, hence, larger buckling.

The arguments presented above also explain configuration O1Zr', the lowest-energy structure of the compressed-oxide (B) calculations. It is similar to O1Zr, which optimizes the O1–Zr(S) interaction by placing these two atoms on top of each other. A small (30–40 pm) lateral shift still leaves this bond almost unchanged, but helps to shorten one of the Zr–Pd$_{Sj}$ bonds.
bonds. This is also reflected by the other structural parameters in table 3, which are almost unaffected except for the Zr buckling in the oxide: the stronger Zr–Pd$_{3Zr}$ interaction drags this Zr atom in the oxide further down towards the Pd$_{3S}$. To determine whether the differences between the ZrO$_2$ trilayers on Pt/Pt$_3Zr$ and Pd$_3Zr$ are only due to the presence of Zr$_{3S}$ at the interface or also caused by the chemical differences between Pt and Pd, we also investigated ZrO$_2$ on a hypothetical Pt-terminated Pd$_3Zr$ substrate. The geometries of ZrO$_2$/Pt/Pt$_3Zr$ and ZrO$_2$/Pd/Pd$_3Zr$ are essentially the same. The differences of interlayer distances and oxide buckling amplitudes are ≤3 pm, with the exception of the O1–substrate interlayer distance, which is smaller by 10–15 pm for ZrO$_2$/Pd/Pd$_3Zr$. The oxide is also bound ≈35 meV more strongly on Pd/Pd$_3Zr$. These differences are, however, small compared to the consequences of having Zr in the uppermost layer of the substrate, as found in the real ZrO$_2$/Pd$_3Zr$ trilayer oxide: compared to the hypothetical Pd-terminated substrate, the adsorption energy increases by more than 1/3.

Finally, STM simulations of our vdW-DF model structures using the Tersoff–Hamann approach [51] were performed (using the substrate lattice parameter). The simulated STM images predict that the protrusions seen in STM are related to the upwards-buckled Zr atoms. The O2 atoms also contribute to the local density of states (LDOS) above the surface. Thus, the LDOS maxima are located somewhere between the Zr and O2 atoms. The large Zr buckling is reflected in the apparent heights of these atoms, with the lower ones not appearing as protrusions at all. This is consistent with the experimentally observed large buckling in atomically resolved STM images. It also implies that the protrusions in images like figure 5(b) correspond to the Zr atoms as the buckling of the O2 layer is much less. In contrast to the calculated STM images, in figure 5(b) all Zr atoms are visible as protrusions. This indicates that tip-sample interaction plays an important role, which is beyond the applicability of the Tersoff–Hamann model. Considering that the imaging conditions used for figure 5(b) would imply a low tip-sample distance even on a conductor, significant tip-sample interaction should be expected at these conditions for an insulating surface. Nevertheless, a comparison of the ZrO$_2$ films on Pd$_3Zr$ and Pt$_3Zr$ shows the correct trends: STM simulations for the more weakly bound ZrO$_2$/Pt/Pt$_3Zr$ trilayer show much less contribution from O2, i.e. there the Zr atoms stand out more prominently in the simulated images. This difference in the LDOS is also reflected in experiments: it is easier to obtain STM images with atomic resolution for ZrO$_2$/Pt/Pt$_3Zr$ than for ZrO$_2$/Pd$_3Zr$, and the Zr atoms appear more well-defined in experimental images of ZrO$_2$/Pt/Pt$_3Zr$.

5. Discussion and conclusion

Oxidation of Pd$_3Zr$(0001) under suitable conditions creates a zirconia film similar to the one formed by oxidation of Pt$_3Zr$(0001). The film is an O-Zr-O trilayer, equivalent to the (1 1 1) termination of cubic zirconia. The in-plane lattice parameter is 351.2 ± 0.4 pm, very close to that of the equivalent oxide on Pt$_3Zr$(0001) [16], and 3% less than for bulk-like ZrO$_2$(1 1 1). In spite of distinct bonds between the oxide and the substrate, the film is at least close to incommensurability. At first glance, one might attribute this to the stiffness of the film towards in-plane deformation, which does not allow it to adjust its lattice constant as would be enforced by a small commensurate cell. We must note, however, that a much smaller ($\sqrt{3} \times \sqrt{3}$)R8.9° cell would be possible with exactly the same oxide lattice parameter as the large ($\sqrt{217} \times \sqrt{217}$)R10.16° cell, but with a different rotation (8 or 26°) between the oxide and the substrate (experimental value 12.3°). This indicates that the local bonding geometry, correlating the up and down buckling between neighboring oxide cells, is more important than any long-range superstructure periodicity. Possibly, the rotational alignment is related to the moiré vectors being close to a ($\sqrt{3} \times \sqrt{3}$)R30° superstructure.

On Pd$_3Zr$(0001), the substrate layer below the oxide is the stoichiometric alloy, not a Zr-free pure-metal layer as on Pt$_3Zr$(0001). This difference could be a consequence of easier diffusion in Pd$_3Zr$ compared to Pt$_3Zr$: the temperatures needed to form a homogeneous, well-ordered oxide film are 850–900 °C for both substrates, while the melting temperature of Pd$_3Zr$ is lower (2326 °C for Pd$_3Zr$, 2700 °C for Pt$_3Zr$). A higher mobility in Pd$_3Zr$ during preparation of the oxide could make it easier to replenish the Zr used for the oxide.

Whether or not the layer beneath the oxide contains Zr is decisive for the differences between the ZrO$_2$ films on the two substrates. On Pt-terminated Pt$_3Zr$, bonding occurs mainly between the Zr atoms of the oxide and the Pt in the substrate [16]. On Pd$_3Zr$, the presence of Zr in the surface layer leads to the formation of strong O1–Zr$_{3S}$ bonds. These strong bonds lead to large distortions of the film. In particular the Zr layer in the oxide shows high buckling that is also reflected in the experimental STM images. DFT indicates that the distortions of the film might even locally break O–Zr bonds in the oxide (O1Pd geometry in figure 6). We consider it possible that such local disruption of the ZrO$_2$ film is responsible for the uneven appearance of STM images, as in figure 5(a) (dark spots), and the absence of a perfect superstructure cell observable in STM.

Comparing the practical use of the two substrates for growing ultra-thin ZrO$_2$ films, Pd$_3Zr$ has the advantage of easier crystal growth and therefore lower cost. In contrast to Pt$_3Zr$, Pd$_3Zr$ does not suffer from problems with domain boundaries when preparing the clean alloy. This is again attributed to easier diffusion and, hence, better equilibration of the stoichiometry in Pd$_3Zr$. In addition, the pure Pt layer below the ZrO$_2$ film on Pt$_3Zr$ reconstructs, causing spatial inhomogeneity and metal islands below the oxide; neither are present for ZrO$_2$/Pd$_3Zr$(0001). The main disadvantage of Pd$_3Zr$ is the formation of large oxide clusters (with undefined properties and which are detrimental for imaging by STM). Pt$_3Zr$ is more benign in this respect. We attribute this problem to easier dissolution of oxygen in Pd$_3Zr$. As soon as a closed oxide film has formed, O$_2$ does not dissociate on the film (self-limited oxidation). Oxygen diffusing from the bulk is not affected by this limitation and leads to further oxidation of Zr. The extra oxide forms clusters rather than a multilayer oxide of uniform thickness. This phenomenon is reminiscent of Stranski–Krstanov growth in deposition, and the reason is probably the same: the trilayer oxide is energetically more
favorable than a thicker oxide because it can better adapt to the substrate. For a thicker oxide, large distortions such as the buckling of the Zr layer are less favorable, but these distortions are necessary to optimize bonding to the substrate. Compared to an oxide film with uniform thickness, oxide clusters reduce the interface area where the substrate–oxide interface energy is less favorable than that in the trilayer oxide.

For an STM study, the larger buckling of the oxide on Pd3Zr has some disadvantages. Adatoms or molecules with a small apparent height do not stand out as clearly in STM images as on ZrO2/Pt/Pt/Zr(0001). On the other hand, when comparing the ZrO2 films on these two substrates, the oxide films hardly differ except for the different buckling. Considering the different ZrO2 bulk structures, we have to note that the cubic ZrO2 phase should not exhibit any buckling at the (1 1 1) surface, while {1 1 1} layers of monoclinic ZrO2 show buckling of the Zr layers between 12 and 112 pm already in the bulk, depending on the orientation. Therefore, comparing the ZrO2 films on Pd3Zr and Pt/PtZr provides the opportunity to study the effect of geometry on the chemical properties of the oxide. This is especially valuable considering the variety of different ZrO2{1 1 1} surfaces: at least with respect to geometry, ZrO2/Pd3Zr may be regarded as a model system for the study of unbuckled cubic ZrO2.

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