Structure of ultrathin Pd films determined by low-energy electron microscopy and diffraction

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Abstract. Palladium (Pd) films have been grown and characterized \textit{in situ} by low-energy electron diffraction (LEED) and microscopy in two different regimes: ultrathin films 2–6 monolayers (ML) thick on Ru(0001), and \textasciitilde 20 ML thick films on both Ru(0001) and W(110). The thinner films are grown at elevated temperature (750 K) and are lattice matched to the Ru(0001) substrate. The thicker films, deposited at room temperature and annealed to 880 K, have a relaxed in-plane lattice spacing. All the films present an fcc stacking sequence as determined by LEED intensity versus energy analysis. In all the films, there is hardly any expansion in the surface-layer interlayer spacing. Two types of twin-related stacking sequences of the Pd layers are found on each substrate. On W(110) the two fcc twin types can occur on a single substrate terrace. On Ru(0001) each substrate terrace has a single twin type and the twin boundaries replicate the substrate steps.
1. Introduction

Palladium (Pd) is a component of many structural materials, electronic materials and commercial catalysts [1]. The functionality of these materials is engineered in several ways, including the use of nanocrystalline or nanoparticle forms and by combining Pd with other metals, either in an alloy or in core–shell structures. In addition, the properties can be optimized by inducing strain and defects such as stacking faults. Some such ‘modified’ forms of Pd have been experimentally confirmed to present ferromagnetic order [2, 3]. Ferromagnetism in Pd has been shown in theoretical studies to be greatly affected by stacking faults and twin boundaries [4]. Given this background, it is important to completely characterize the structure of Pd in various forms. Here we explore the structural properties of Pd as ultrathin films supported on metal substrates. Thin films offer several advantages in structural characterization, relative to, for example, core–shell or alloy nanoparticles. Specifically, low-energy electron diffraction (LEED) can be used to determine the surface structure.

In this work, we present a detailed LEED and low-energy electron microscopy (LEEM) characterization of both thin films, in the range of 2–6 monolayers (ML) Pd on Ru(0001), as well as of the surface of ‘thicker’ films, ~20 ML thick, grown on both Ru(0001) and W(110). The latter could be considered structurally as a proxy for bulk Pd(111) surfaces.

Pd on Ru(0001) has been studied previously by several groups, focusing on the monolayer limit. A Pd monolayer on Ru(0001) is pseudomorphic with the substrate. Alloying is not detected if the growth is performed at room temperature (RT) or below [5]. At higher temperatures, alloying can occur. For example, at 870 K alloying at the edge of the growing Pd islands hinders further growth, producing distinctive labyrinthine islands [6]. Further annealing to 1150 K produces a uniform bidimensional alloy of PdRu [5]. Thicker films do not grow layer-by-layer [7] at RT or below. In the same study using reflection high-energy electron diffraction, x-ray photoelectron spectroscopy and x-ray photoelectron diffraction, the three-dimensional growth of Pd/Ru presented a twinned fcc structure with an unusual subsurface expansion of up to 7% in the second and third Pd layers in a film of 5 ML average thickness.

The surface of Pd(111) single crystals has been the subject of several structural studies [8, 9]. Unlike most transition metals, LEED experimental determinations of the last-layer interlayer spacing give a slight expansion instead of a contraction. This expansion could be caused by residual hydrogen adsorbed on the surface, as suggested for several transition metals [10]. We also compare our thin-film interlayer separations with \textit{ab initio} calculations.
2. Experimental and theoretical details

All the experiments were carried out in situ in an ultra-high vacuum Elmitec III low-energy electron microscope [11]. The instrument allows monitoring growth in real time, as well as imaging while the sample is exposed to gases or during heating/cooling between 200 and 1600 K. The base pressure of the system is $1 \times 10^{-10}$ Torr. The Ru(0001) and W(110) substrates were cleaned by exposure to $1 \times 10^{-8}$ Torr of O$_2$ at 890 K, followed by brief flashes to 1600 K. Pd was deposited from a Pd rod heated by electron bombardment. During the growth of the films, the pressure remained in the $10^{-10}$ Torr range. Typical deposition rates were 0.3 ML min$^{-1}$. Films up to about 6 ML were produced in a layer-by-layer growth mode at elevated temperature, with the local film thickness determined by counting the layers as they grew using layer-thickness contrast from the quantum size effect (QSE). Films around 20 ML thick were grown by calibrating the deposition rate needed to complete a 1 ML Pd film on Ru(0001).

To check for the presence of crystallographic twin structures in the films, dark-field images were acquired in addition to the regular bright-field images. The latter are created from the specular beam. The dark-field images were formed from one of the first-order diffraction beams (i.e. a (01)-type beam), which gives contrast between fcc twin structures in the Pd films at certain electron energies.

LEED was performed with the LEEM instrument, which allows acquiring selected area diffraction patterns and intensity versus energy (IV) data of areas as small as half a micrometer by means of an aperture that limits the electron beam size on the sample [12]. We measured IV curves for the specular beam and each of the three equivalent (01) and (10) beams in the range of 50–350 eV, with a total energy range of 900 eV. All LEED IVs were acquired either at 200 K or at RT. In the particular case of 6 ML Pd on Ru, diffraction data were obtained for several different temperatures between 200 and 480 K. Within measurement error, no difference was detected in the lattice spacings as a function of temperature.

Multiple-scattering LEED IV calculations were performed with a modified version of the van Hove–Tong package [13–16]. The surface was modeled by stacking the necessary number of Pd layers over five layers of Ru(0001) or W(110) bulk using the renormalized forward scattering approach. For films on Ru(0001), the diffraction data came from a single Ru terrace, and in the thinner films (up to 6 ML), from a single Pd thickness. For W(110) (see section 3.3), the Pd films contained twin domains within W terraces even for our smallest analysis region. In this case, an incoherent mixture of domains was used in the calculations and the ratio of domain types was used as a free parameter. The interlayer spacings of the close-packed planes parallel to the surface were explored by calculating the IV curves over a three-dimensional (3D) parameter grid. The interlayer spacings were swept over wide ranges. The LEED theory–experiment agreement was quantified by Pendry’s $R$ factor, $R_p$ [17]. The error bars for each parameter were obtained from its variance. Correlations between the structural parameters were taken into account for the estimation of the error limits. All the structural parameters derived present well-defined minima in their respective $R_p$ factor plots.

We have also addressed the structure of the Pd films from a purely theoretical approach by performing total energy calculations with the ab initio code SIESTA, which is based on density functional theory (DFT) [18, 19]. The Pd films were modeled by stacking two, three and four Pd layers on top of a four-layer thick Ru ($1 \times 1$) slab oriented along the (0001) direction. We assumed perfect epitaxy so that the combined Ru+Pd system has a ($1 \times 1$)
periodicity with respect to the Ru(0001) 2D unit cell. While the Ru stacking was fixed to
the hcp sequence, we surveyed all possible stacking sequences for each Pd film thickness.
In the geometry optimizations all atoms except those in the last two Ru layers were allowed
to relax until atomic forces were lower than 0.02 eV Å\(^{-1}\). For the total energy calculations,
we employed scalar-relativistic norm-conserving pseudo-potentials \([20]\) for Pd and Ru and a
double-zeta polarized basis set of localized numerical atomic orbitals. Both the local density
approximation (LDA) \([21]\) and the generalized gradient approximation (GGA) \([22]\) were tested
for most configurations. Brillouin zone integration was performed over a \((15 \times 15)\) grid in
\(k\)-space. We will only present the LDA results because they reproduce more accurately the
bulk experimental lattice constants for both metals: for hcp Ru \(a_{\text{exp}} = 2.71 \text{ Å}, a_{\text{LDA}} = 2.71 \text{ Å}, a_{\text{GGA}} = 2.74 \text{ Å}\) and for fcc Pd \(a_{\text{exp}} = 3.87 \text{ Å}, a_{\text{LDA}} = 3.88 \text{ Å}, a_{\text{GGA}} = 4.00 \text{ Å}\) \([23]\). Nevertheless,
our conclusions, in terms of normalized expansion of the interlayer distances, are unchanged if
the GGA is employed instead.

3. Results and discussion

Our principal diagnostic in this report, LEED IV, has the fewest possible interpretations if the
diffraction data are obtained from a uniformly thick film on a single substrate terrace. Using
our instrument, these regions need to be roughly a micron in size. However, the fcc structure
of bulk Pd has an in-plane (111) spacing of 2.75 Å, which is 1.7% larger than the Ru(0001) in-
plane spacing \([23]\). This lattice mismatch should promote 3D growth, and prevent the formation
of uniform-thickness, smooth films. Such 3D growth has been reported at room temperature
or lower temperatures \([7]\). However, the lattice mismatch might be able to be accommodated
elastically in films up to several layers thick on Ru(0001). There is agreement that monolayer
Pd films on Ru(0001) are pseudomorphic, i.e. they are lattice matched to the Ru substrate \([5, 6]\).
Thicker films are expected to eventually relax towards the bulk in-plane value.

There are several strategies to obtain flat films in systems that prefer to grow 3D islands.
One is to tailor the growth parameters and use large terraces on the substrate, taking advantage
of kinetic limitations to nucleate new layers on top of existing islands \([24]\). Another method
is to dose the film material at room or lower temperature, producing a rough and disordered
but continuous film. After the growth, the film is annealed to improve the smoothness and
crystallinity. With care, the film can be smoothed before it dewets and forms three-dimensional
islands \([25]\).

Using the \textit{in situ} and real-time ability of LEEM allows us to explore the parameters that
promote smooth films, including the flux and/or temperature for thin films or the time and
temperature during annealing of thicker RT-grown films. We first discuss thin-film growth, and
then present the results on the thicker, annealed films.

3.1. Pseudomorphic Pd films on Ru(0001)

By growing Pd on large Ru terraces, i.e. terraces larger than a few micrometers, a layer-by-
layer growth front can be achieved using a substrate temperature of 750 K and a flux rate of
0.25 ML min\(^{-1}\). Figure 1 shows frames from a continuous movie selected to show the nucleation
of each new layer up to 7 ML thick. The initial substrate, figure 1(a), presents a terrace of nearly
8 µm across (thicker gray lines indicate step bunches around the central terrace, whereas thinner
gray lines correspond to monatomic steps).
Figure 1. (a)–(l) LEEM images selected from a real-time movie acquired during the growth of Pd on Ru(0001). The field of view is 9.3 \( \mu \text{m} \).

The growth starts by Pd islands decorating the substrate steps and by the nucleation of roughly triangular islands in the middle of the terrace (figure 1(b)). Before the first layer is completed, the second and third layers (black islands in figure 1(e)) start to nucleate on top of the first and second layers, respectively (figures 1(d)–(f)). The dendritic shape of the edges of the first layer islands probably result from some alloying at island edges [6]. Thicker islands have smoother edges (figures 1(g)–(l)).

The contrast between film regions of different thickness is due to a QSE on electron reflectivity [11]. To quantify these changes, we present in figure 2 the complete electron reflectivity of areas between 2 and 6 ML thick, acquired in different films (as the films only expose at most three different layers each). The intensity was recorded from bright-field LEEM images by measuring the reflected electron intensity from a given Pd terrace as a function of incoming electron energy. The reflectivity is dominated by a broad peak around 20 eV. This
Figure 2. Electron reflectivity curves acquired on areas of labeled Pd thickness of Ru(0001).

Figure 3. (a) LEEM image taken after the growth of Pd on Ru(0001). The field of view is 14.5 µm. (b) At 141 eV, the LEED pattern of a 6 ML Pd area on a single Ru(0001) terrace, marked in (a) with a circle, has three-fold symmetry. (c) At 132 eV, the LEED pattern from the same Pd region has roughly six-fold symmetry.

peak is attributed to the forbidden gap of the (222) Bragg reflection [26]. The smaller peak that appears in all the films close to 16 eV is probably due to a bulk-bands crossing [26], although it has also been assigned to a Tamm resonance [27] or an anisotropy effect in electron inelastic scattering [28]. The other oscillations detected in the thinner regions correspond to QSEs due to interference between electron reflection at the film surface and at the Pd/Ru interface. The sharpness of the oscillations suggests that the latter interface is abrupt and free of significant alloying.

In figure 3, we present the LEED pattern acquired from a uniformly thick region of 6 ML on a single Ru terrace. The selected-area LEED patterns of all the thicknesses from 2 to 6 ML Pd
show only integer (first-order) \((1 \times 1)\) spots at the same positions as the original substrate spots within our experimental resolution, which we estimate to be \(\pm 2\%\). Since the in-plane lattice spacings of bulk Pd and bulk Ru differ by 1.7\%, this resolution is insufficient to prove that the films have the same exact lattice spacing as the substrate. Nevertheless, the 2–6 ML films do not have satellite beams, which would be expected from multiple scattering between differently sized Pd and Ru lattices. A further proof of the in-plane matching of the films to the substrate comes from LEED IV, as discussed below. Thus, the films are pseudomorphic with the substrate, i.e. the Pd unit cell is distorted in-plane in order to obtain a one-by-one correspondence with the substrate atoms. This implies that Pd films up to 6 ML on Ru are under a 1.7\% compressive strain. This compression should expand the film’s interlayer spacing relative to the bulk value. A simple estimate of the effect can be made by assuming that the Pd layers want to maintain the bulk nearest-neighbor distance to the atoms in adjacent layers even though they are compressed in-plane. This model predicts an interlayer separation of 2.26 Å for the strained films, slightly larger than the bulk value of 2.25 Å.

Even if Pd is fcc in bulk, there is the possibility of having different stacking sequences or stacking faults when in thin-film form. This possibility is more likely, given that the Ru(0001) substrate is hcp and that the first Pd layer grows following the same sequence [5]. The symmetry of the LEED pattern is three-fold for all thicknesses from 2 to 6 ML. However, this three-fold symmetry alone does not allow distinguishing between fcc and hcp Pd\(^5\). We next use the LEED IV data to determine the layer stacking sequence in the Pd films. We will use the common naming scheme of a, b, c to indicate each of the three possible hexagonal layers for a close-packed structure. When needed, we will denote the substrate layers with uppercase labels ABAB, and the film layers with lowercase acba, with the rightmost letter always indicating the topmost layer. For example, we will denote an fcc structure by acb and its twin (mirror fcc) as bca. Additionally, it is helpful to use Frank’s notation [29] where the stacking of a layer relative to the one below is labeled. Transitions of one layer to the next following the sequence \(A \rightarrow B \rightarrow C \rightarrow A\) are denoted by \(\nabla\), whereas the opposite transitions, namely \(C \rightarrow B \rightarrow A \rightarrow C\), are denoted by \(\Delta\). An fcc structure is written as either \(\Delta\Delta\Delta\) or \(\nabla\nabla\nabla\). An hcp structure corresponds to \(\Delta\nabla\Delta\nabla\).

Since LEED IV curves (see figure 4) were obtained from regions of uniform thickness on a single substrate terrace, we can directly determine how Pd is stacked on Ru. We start discussing the bilayer of Pd, the film most likely to deviate in layer stacking from bulk Pd due to substrate interactions. Considering both possible terminations for a Ru terrace, BABA or ABAB \((\nabla\nabla\Delta\Delta\) and \(\Delta\nabla\Delta\nabla\), respectively), together with all possible sequences of Pd layers, the best fit found corresponds to ABAB/ac \((\Delta\nabla\Delta\nabla/\Delta\Delta)\), with \(R_p = 0.15\) (all the other models result in a much worse \(R_p > 0.50\)). The fit shows a strong sensitivity to bulk Ru orientation, allowing us to establish unambiguously the ABAB termination of the Ru terrace where the LEED pattern was acquired. The interlayer spacings for the 2 ML case are shown in table 1. It is noteworthy that the topmost two Ru layers are contracted by 4\% relative to bulk Ru, similar to bare Ru(0001) [12]. The distance between Pd layers is very close to the value for a slightly compressed Pd layer that we estimated above. Thus, even just two layers of Pd behave as expected for thicker films pseudomorphic to Ru.

For 3 ML the best fit is ABAB/acb \((\Delta\nabla/\Delta\Delta\Delta)\), with \(R_p = 0.16\). In the same way, for films up to 6 ML Pd, the best fit always corresponds to an fcc stacking sequence. The interlayer

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\(^5\) LEED from a single terrace of an hcp metal is also three-fold [12].
Table 1. Structural parameters for the LEED IV best fit for 2 ML of Pd on Ru(0001). Interlayer spacings are given in angstrom. Subscripts number the Pd layers starting from the surface and the Ru layers starting from the film/substrate interface. The stacking sequence is described in both hexagonal layer and Frank’s notation.

| 2 ML Pd/Ru |   |
|------------|--|
| ABac       |--|
| △▽/△△      |--|

| Pd₁Pd₂     | 2.26 ± 0.02 |
| Pd₂Ru₁     | 2.22 ± 0.04 |
| Ru₁Ru₂     | 2.04 ± 0.05 |
| Rₚ         | 0.15 ± 0.03 |

Figure 4. LEED IV data and best fit to (a) 2 ML Pd/Ru(0001) and (b) 6 ML Pd/Ru(0001).

spacings are reported in table 2. For all the films, the interlayer spacings of the topmost two layers are not contracted (or very slightly, and well within the error bar) relative to deeper layers. This lack of contraction is similar to previous Pd(111) LEED results [8, 9] that indicated no significant contraction of the last Pd layer, in contrast with other transition metals [10]. To check for possible hydrogen contamination that could potentially remove the last Pd layer contraction [30], we acquired LEED IVs for a 6 ML Pd film at 480 K. Hydrogen is known to desorb from Pd at temperatures far below 480 K [31]. The interlayer spacing for the first layer was still 2.27 Å.

As a further check on the in-plane lattice spacing of Pd films, we performed a LEED IV fit to the data from the 6 ML Pd film varying the in-plane Pd spacing. (The previous fits were all performed at the Ru in-plane spacing.) This film is the best candidate for detecting any in-plane relaxation. As figure 5 shows, the fit has a well-defined minimum at about 2.70 Å, close to the

We have not considered an energy dependence of the real part of the inner potential [32]. In any case, we are not approaching the 0.01 Å error level, where such omission gives rise to systematic errors.

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Table 2. LEED IV best-fit structural results for the interlayer spacing for different Pd areas. All distances are in angstrom. Each stacking sequence is described in both hexagonal layer and Frank’s notation.

| Pd area | 3 ML Pd/Ru | 4 ML Pd/Ru | 5 ML Pd/Ru | 6 ML Pd/Ru |
|---------|-------------|-------------|-------------|-------------|
|         | ABac | ABacb | ABacba | ABacbac | ABacbacb |
|         | △▽ / △△△ | △▽ / △△△△ | △▽ / △△△△△ | △▽ / △△△△△△ |
| Pd1Pd2  | 2.29 ± 0.02 | 2.26 ± 0.03 | 2.28 ± 0.03 | 2.27 ± 0.02 |
| Pd2Pd3  | 2.27 ± 0.05 | 2.28 ± 0.05 | 2.28 ± 0.05 | 2.27 ± 0.05 |
| Pd3Pd4  | 2.24 ± 0.06 | 2.26 ± 0.06 | 2.28 ± 0.06 | 2.28 ± 0.06 |
| Rp      | 0.16 ± 0.04 | 0.14 ± 0.03 | 0.18 ± 0.05 | 0.17 ± 0.04 |

Figure 5. Pendry’s $R_p$ factor describing the fit quality for varying in-plane distance of a 6 ML Pd region on Ru(0001). The lines are a guide to the eye.

in-plane spacing of bulk Ru (2.704 Å) but well resolved from the spacing of bulk Pd (2.75 Å). Using the LEED patterns and the LEED IV fits to the experimental data, we find that the films grown layer-by-layer are pseudomorphic up to at least six atomic layers.

The ab initio calculations predict geometries very similar to those determined from the experimental LEED IV data. The lowest energy configuration for 2 to 4 ML Pd on Ru(0001), with the in-plane Ru lattice spacing, is an fcc stacking within the Pd layers, with a very small expansion of the last Pd layer. The interlayer distances are presented in table 3. Thus, both experiment and theory lead us to conclude that the last-layer slight expansion of Pd films is not a contamination effect but rather an intrinsic property of the clean Pd surface.

Even if the layer stacking we detect by LEED IV is a unique fcc sequence on a single terrace, we next establish that the film has a twinned fcc microstructure due to the substrate.
Table 3. Interlayer spacing from DFT calculations for different thickness; distances are in angstrom. ‘PdRu’ refers to the layer separation at the film/substrate interface.

|                 | 2 ML Pd/Ru | 3 ML Pd/Ru | 4 ML Pd/Ru |
|-----------------|-----------|-----------|-----------|
|                 | ABac      | ABacba    | ABacba    |
| Pd<sub>1</sub>Pd<sub>2</sub> | 2.27      | 2.29      | 2.28      |
| Pd<sub>2</sub>Pd<sub>3</sub> | 2.20      | 2.27      | 2.27      |
| Pd<sub>3</sub>Pd<sub>4</sub> | 2.21      | 2.27      |           |
| Pd<sub>4</sub>Pd<sub>5</sub> |           | 2.21      |           |
| PdRu            | 2.09      | 2.09      | 2.09      |

The Ru substrate is hcp, i.e. ABAB, so the exposed basal plane alternates at adjacent terraces separated by monatomic steps. That is, the Ru termination is either A or B. This causes the preferred fcc stacking of the Pd to rotate by 180° across consecutive substrate terraces, giving a LEED pattern that also rotates by 180° [12]. Frank’s notation is useful in this respect as the orientation of the LEED pattern from each twin structure is reflected in the orientation of the Frank triangles, as well as making it clearer when the sequence is fcc or hcp. On an ABAB terrace, the Pd stacking sequence as determined by LEED is ABAB/acb (\(\triangle \triangledown / \triangle \triangle \)) and the bc(\(\triangledown \triangledown \triangledown\)) Pd sequences are a mirror image of one another, i.e. twins. Thus, a twin boundary extends from each substrate step, through the film, up to its surface.

A way to directly image the twin microstructure of a Pd film in LEEM is to combine dark-field and bright-field imaging of the same area. Figure 6(a) presents a LEEM image from a film with Pd regions that are 6, 7 and 8 ML thick. Each different thickness has a different gray level due to the QSE on the electron reflectivity mentioned before (figure 2). Dark-field imaging is sensitive to fcc twins. A bca (\(\triangledown \triangledown \triangledown\)) sequence gives the same diffraction pattern as an acb (\(\triangle \triangle \triangle\)) sequence, but rotated by 180°. Hence the (01) and (10) beams will be exchanged by going from one twin to the other. If an energy is selected, where a three-fold symmetric pattern is observed, as in figure 3, then only one set of twins will be imaged if the (01) beam is used for dark-field imaging whereas the other set of twins on the surface will be imaged if the (10) beam is used. This effect can be observed in figures 6(c) and (d).

In contrast, bright-field imaging is not sensitive to the two types of fcc stacking. Figure 6(b) provides an example. To reduce the QSE contrast, the image was acquired very close to the forbidden gap corresponding to the (222) Bragg reflection, at an energy of 18.5 eV. With the contrast from film thickness minimized, it is easy to see that the twin structures on the different Ru terraces have the same contrast. However, bright-field imaging can be sensitive to stacking mistakes in the Pd film on a given Ru terrace. Figure 6(b) shows an example. The only area with a markedly different contrast is the small region of 8 ML Pd marked with an arrow. Such regions occur with very low density. The schematic of figure 6(e) presents a model of the stacking fault that makes the region special<sup>7</sup>. As it has a non-fcc structure, its vertical periodicity is different.

<sup>7</sup> The stacking-fault schematic shows only the topmost Pd layer being faulted compared to the Pd on the same Ru terrace. The fault can possibly lie deeper into the film.
from the fcc areas, and the forbidden gap corresponding to the (0002) hcp structure appears at a different energy from the rest of the fcc film. A similar effect has been observed in Co islands on Ru(0001) [33]. The stacking-fault region also has contrast in the dark-field images. In figure 6(c), for example, the region has roughly the same contrast (brightness) as the 7 ML Pd on the higher terrace to the immediate left. The similar contrast is explained by the same stacking sequence of the last two layers of the stacking-fault region and of the Pd on the upper terrace with a twin fcc structure (see figure 6(e)), as indicated by Frank’s notation. One effect observed in the thicker pseudomorphic films is the presence of linear defects, as best seen in the bright-field images in figures 6(a) and (b). These defects are likely the precursor of a dislocated interface layer, or they might even be small film regions with a dislocated interface layer.

In summary, thin films of up to 6 ML Pd on Ru(0001) grown at elevated temperature have the in-plane lattice spacing of Ru(0001). They present a twinned fcc microstructure, where each substrate terrace has a single twin, except for rare stacking faults. The substrate steps are then replicated into twin boundaries, which run through the film. The film’s vertical lattice spacing is
Figure 7. LEEM image acquired during the initial stage of depositing $\sim 20$ ML Pd on an RT Ru(0001) substrate at a rate of 0.60 ML min$^{-1}$. The image size is 2.25 $\mu$m. The same image contrast is used for all the images.

slightly expanded, as expected due to the in-plane compressive strain. No significant last-layer contraction is detected, in agreement with $ab$ initio calculations and with previous reports on single-crystal Pd(111) surfaces [8, 9].

3.2. Relaxed Pd films on Ru(0001)

To obtain a surface more akin to a Pd(111) single crystal, $\sim 20$ ML Pd layers were deposited at RT on Ru(0001). The initial stages of the growth are followed in figure 7. During dosing up to half a monolayer, a granular texture was observed in the LEEM images, which probably results from islands smaller than the in-plane resolution of LEEM (10 nm). With further deposition, the reflected electron intensity gradually decreases due to increased film roughness.

After the growth, the film was annealed to 880 K and cooled back to RT while imaging (figure 8). At the end of the procedure the surface of the film is quite flat, having monatomic Pd steps separated by nearly a micrometer.

As the film is continuous, the diffracting electrons do not see the Ru substrate. Thus, the LEED patterns only provide information for the topmost Pd layers. If acquired on a single substrate terrace, the pattern is still three-fold symmetric, as shown in figure 9(a). In the LEED IV fits, all the models with the three different possible stackings of hexagonal layers of Pd were first explored, initially with a Pd bulk in-plane lattice spacing. The best fit, shown in figure 9(b), is an acb termination, with an $R$-factor $R_p = 0.12$. (The other models yielded $R_p > 0.60$.) The structural parameters are shown in table 4. The first interlayer spacing again shows a very small expansion, with 2.26 Å (within the error bars of the bulk value of 2.25 Å). This is the same result that was previously reported by van Hove et al [8, 9] for a Pd(111) single-crystal surface.

The in-plane lattice spacing of the thick, annealed Pd film was determined by finding the value in the multiple-scattering calculations that best fits the experimental LEED IV curves.
Figure 8. LEEM images of the same area: (a) before Pd growth at RT, (b) after \(\sim 20\) ML Pd growth at RT and (c) after annealing to 890 K. The field of view is 14.5 \(\mu m\).

Figure 9. (a) LEED pattern of thick \(\sim 20\) ML Pd film on Ru(0001) at 53 eV, acquired from a single Ru terrace. Note the three-fold symmetry. (b) Experimental LEED IV curves and best fits.

Figure 10 shows that the Pendry \(R_p\) factor is optimized at about 2.75 Å, i.e. the value for bulk Pd within the error limits of the fits. Thus, the thick film is relaxed in-plane, unlike the thinner films grown at elevated temperature, which had the Ru in-plane spacing (2.704 Å).

After the annealing, some of the surface film steps are located at positions close to the substrate steps. This observation is revealed by comparing the location of the bare Ru steps (the thin, dark lines in figure 11(a)) and the Pd steps (the thin, dark lines in figure 11(b)). In addition,
Table 4. Interlayer spacing and stacking sequence of a uniform thickness region of a ∼20 ML Pd film on Ru(0001), as determined from the best LEED IV fit. Distances are in angstrom.

| ∼20 ML Pd/Ru | acb | Δ |
|---------------|-----|---|
| Pd_1/Pd_2   | 2.26 ± 0.02 |   |
| Pd_2/Pd_3   | 2.22 ± 0.04 |   |
| Pd_3/Pd_4   | 2.26 ± 0.05 |   |
| R_p          | 0.12 ± 0.02 |   |

Figure 10. Pendry’s $R_p$ factor describing the fit quality of a thick ∼20 ML annealed Pd film on Ru(0001) for varying in-plane distance.

new Pd steps are located at other locations of the surface. The conformal nature of the film, with many of its steps nearly over substrate steps through 20 film layers, surprises us.

Twin structures are still expected in the thick film since the two twin-related fcc stacking sequences of Pd layers have the same energy. To check for their presence, dark-field LEEM images were acquired at the same location as the bright-field images of figures 11(a) and (b). Figure 11(d) shows the dark-field LEEM images acquired with two different energies. Inspection shows that the regions of bright/dark contrast uniquely correspond to Ru terraces separated by monoatomic Ru steps. Thus, like the thinner films, the thick film also has a single unique stacking of Pd layers on each Ru terrace. Substrate steps are replicated into the film as twin boundaries. While the substrate steps were smooth, the twin boundaries are more jagged,
Figure 11. (a) LEEM image of the Ru(0001) substrate before Pd deposition. The image size is 8.9 µm. (b) LEEM image after depositing ~20 ML of Pd and annealing. (c) LEED pattern of a single substrate terrace. (d) Dark-field LEEM images of the same area taken with the (10) spot using two different energies that reverse the contrast (upper, 29.3 eV and lower, 42.5 eV).

probably because they have lower energy for the selected orientations. The observation that the underlying substrate terraces still dictate the twin distribution is surprising for two reasons. First, small twins within a single Ru terrace might be expected to form when growing the film at low temperature. Second, as the films relax to the in-plane lattice spacing, a network of lattice dislocations near the film/substrate interface should develop. This network adapts the lattice
spacing of the substrate to the lattice spacing of the film. A misfit dislocation network would be expected to decouple the stacking sequence of the Ru substrate and the Pd film. Yet, after annealing, each Ru terrace has a single, unique stacking of Pd layers.

The film is too thick to show in LEED any sign of such a dislocation network. This in turn leaves open the question of whether the dislocation network adapts the lattice spacing abruptly at the Pd/Ru interface, as has been observed for Cu/Ru(0001) [34] and Co/Ru(0001) [33], or through a layer of intermediate density, like in Ag/Ru(0001) [35]. The latter is more probable, given that Pd/Ru is under compressive stress like Ag/Ru(0001) [35]. Further work, likely with information provided by scanning tunneling microscopy, is needed to address the structure of the relaxed Pd/Ru(0001) interface.

In summary, thick films grown at RT and annealed present an in-plane lattice spacing very close to bulk Pd. The behavior of the last-layer expansion agrees well with the results for Pd(111) single crystals [8, 9], which have few fcc twins. In contrast, Pd films on Ru have very high densities of fcc twins: each substrate step has a twin boundary above it, which separates fcc twins on adjacent substrate terraces. The abundance of twins merits further study regarding their possible influence on Pd ferromagnetism [4], especially given the relaxed in-plane spacing of these films.

3.3. Relaxed Pd films on W(110)

W(110), the most compact surface of bcc tungsten that consequently usually presents the largest terraces [36], has often been used for Pd growth [37]–[39]. The growth is known to proceed through an interface layer with a complex arrangement [37] that acts as a buffer between the (110) bcc and the (111) fcc structures of W and Pd, respectively. Attempting to grow thicker films layer by layer will produce 3D islands on top of the interface layer. In order to obtain continuous films, we follow the same recipe as for thick Pd films on Ru(0001): depositing Pd at RT, followed by a brief annealing to 880 K.

Figure 12(a) shows the LEED pattern acquired from the area of a 20 ML film circled in figure 12(b). The LEED pattern is six-fold symmetric. The LEEM images are dominated by wide, diffuse dark lines that form closed loops. They do not show any clear relationship with the pre-existing substrate steps. They also look thicker than the Pd steps observed on Ru(0001) (see figure 11(b)) and present a high curvature. We used dark-field imaging to identify the origin of these lines. A dark-field image from the same area, figure 12(c), exhibits bright and dark regions, which result from fcc twins. The contrast is reversed at a different electron energy (figure 12(d)). Inspection of figure 12 shows that the wide lines of the bright-field image are the boundaries between fcc twins in the dark-field images. Higher temperature annealing led to larger twin domains. Thus, Pd films on both W(110) and Ru(0001) contain high twin densities.

The twins also explain the six-fold symmetry of the LEED pattern in figure 12(a)—the selected area contains both twin types. To perform a multiple-scattering calculation fit, the LEED IV curves were acquired from the full area of figure 12(b). The (10) and (01) beams, shown in figure 13, are very similar, indicating that the two twin structures have similar abundance. The fit was performed by averaging incoherently the two twin fcc stacking sequences, with their ratio as a free parameter. The best fit ($R_p = 0.13$) yields a relative twin population of $40 \pm 20\%$ in the film. For comparison, the ratio observed in dark-field LEEM images is $\approx 55\%$, in good agreement with the estimate from the LEED IV data. The structural
Figure 12. Characterization of thick (∼20 ML) Pd film on W(110). (a) LEED pattern. (b) 7 µm LEEM image. (c, d) Dark-field images of the same region formed from the (1,0) beam at 58.5 and 67.3 eV.

Figure 13. (a) LEED pattern of thick Pd film on W(110) at 53 eV. Note the six-fold symmetry. (b) LEED IV data and best fits.
Table 5. Structural parameters for the best LEED IV fit to the ∼20 ML Pd film on W(110).

| Parameter   | Value           |
|-------------|-----------------|
| 20 ML Pd/W  |                |
| acb + abc   |                |
| △ + \(\nabla\) |                |
| Pd\(_1\)Pd\(_2\) | 2.25 ± 0.03 |
| Pd\(_2\)Pd\(_3\) | 2.20 ± 0.06 |
| Pd\(_3\)Pd\(_4\) | 2.24 ± 0.07 |
| \(R_p\)     | 0.13 ± 0.03    |

Figure 14. Schematics of film microstructures. (a) Pseudomorphic Pd films on Ru(0001). The red line represents a planar twin boundary that starts at the substrate step and runs through the film. (b) Relaxed Pd films on Ru(0001). (c) Relaxed Pd films on W(110).

parameters for the fit are shown in table 5. The interlayer spacing of the two topmost layers, 2.25 ± 0.03 Å, presents a slight expansion (+0.5% compared with bulk Pd interlayer spacing, and within the error limits of no expansion), in line with single-crystal Pd(111) [8, 9] or the films on Ru(0001) presented previously (see tables 2 and 4).

The distribution of twins, as shown in the schematic of figure 14(c), can be explained by considering the nucleation of Pd islands on top of the Pd interface layer. The difference in structure between the interface layer and the subsequent hexagonal layers is so large that the nucleation of the two types of twins is essentially random (similar behavior has been reported for other close-packed metals on W(110), such as Dy or Er [40]). During the initial RT growth, there is a 50% probability of growing one twin or the other. When the film is later annealed, there is a fine distribution of small twins all over the film. The annealing makes the twins coarsen, driven by minimizing the length of the twin boundary. (The twins themselves have the same energy.) This is in contrast with the case of Pd films on Ru(0001), where the two types of substrate terraces provide a preference for one type of twin. In Pd/W(110) the twin distribution evolves very slowly, giving rise to the observed microstructure.
4. Summary

We have grown and characterized ultrathin films of Pd on Ru(0001) and W(110). The structure of the different films is summarized in figure 14. By depositing Pd on Ru(0001) at elevated temperatures, pseudomorphic films can be grown to thicknesses of at least 6 ML. The Pd microstructure replicates the Ru substrate, with an fcc twin on each substrate terrace. Twin boundaries extend from the substrate steps to the film surface. The separation of the topmost Pd layers of each pseudomorphic film is essentially the bulk value. This lack of interlayer contraction is different from the behavior of other transition metal surfaces and does not result from hydrogen adsorption. Thicker films (∼20 ML) were grown at RT and post-annealed, on both Ru(0001) and W(110). This procedure provides films with their in-plane spacing relaxed to the bulk Pd value. The microstructure of thick films on Ru is similar to that of thin, pseudomorphic films: a single twin is detected on each substrate terrace, despite the presumed presence of a misfit dislocation network at the Pd/Ru interface. Again the twin boundaries of the film replicate the step distribution of the substrate. On the other hand, films grown on W(110) present interlocked twins that are difficult to coarsen, and whose distribution has little relation to the substrate steps.

These results indicate that Pd(111) films on Ru(0001) and W(110) are a rich system where the number and location of twin boundaries can be modified or even selected by a proper substrate nanostructuring. We look forward to further studies of the magnetic and chemical properties of these films, especially given the predicted influence of twin boundaries on the magnetic properties of Pd(111) surfaces [4].

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