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Electronic Structure of Pd Multi-Layers on Re(0001): the Role of Charge Transfer

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Abstract. Understanding the origin of the properties of metal-supported metal thin films is important for the rational design of bimetallic catalysts and other applications, but it is generally difficult to separate effects related to strain from those arising from interface interactions. Here we use density functional (DFT) theory to examine the structure and electronic behavior of few-layer palladium films on the rhenium (0001) surface, where there is negligible interfacial strain and therefore other effects can be isolated. Our DFT calculations predict stacking sequences and interlayer separations in excellent agreement with quantitative low-energy electron diffraction experiments. By theoretically simulating the Pd core-level X-ray photoemission spectra (XPS) of the films, we are able to interpret and assign the basic features of both low-resolution and high-resolution XPS measurements. The core levels at the interface shift to more negative energies, rigidly following the shifts in the same direction of the valence d-band center. We demonstrate

that the valence band shift at the interface is caused by charge transfer from Re to Pd, which occurs mainly to valence states of hybridized *s-p* character rather than to the Pd *d*-band. Since the *d*-band filling is roughly constant, there is a correlation between the *d*-band center shift and its bandwidth. The resulting effect of this charge transfer on the valence *d*-band is thus analogous to the application of a lateral compressive strain on the adlayers. Our analysis suggests that charge transfer should be considered when describing the origin of core and valence band shifts in other metal / metal adlayer systems.

Keywords: *d*-band center, core-level shift, Re(0001), Pd thin films

1.   INTRODUCTION

The heterogeneous catalytic activity of multi-metallic systems continues to provide a rich landscape of opportunity in tuning catalytic reaction pathways. By mixing metals to form alloys or composites, new material properties can evolve that can significantly impact performance. Segregation and poor mixing of metals may result prior to or as a consequence of the reaction process itself. In such segregated systems geometric and structural changes with respect to bulk environments can further modify reactivity. A limit case of the separation of metals can sometimes be designed in during synthesis to create core-shell nanoparticles in which a reactive outer skin (often a precious metal) is supported on a core metal (often a cheaper base metal), or as a model system, in the form of a thin metal film supported on another metal. With only a few atomic layers of precious metal, it is typically found that the surface chemical properties are different to that of the bulk metal surface.[1,2] The prediction and rational design of these

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properties has required the development of models of adsorption and reactivity whereby intimate knowledge of the surface electronic structure becomes essential. Thus, a great deal of theoretical and computational work has been devoted to the understanding of these interfaces.[3,4]

The modification of the electronic behavior of metal thin films by the support is produced via a combination of strain and "ligand effects". The former arise because in a supported heterogeneous overlayer system the nearest-neighbor spacing of atoms in the epitaxial layer are unlikely to match those of the bulk of the metal, hence the change in interatomic distances modifies the intra-layer interactions. On the other hand, "ligand effects" are those arising due to the direct interactions between heteroatoms in the system, modifying the electronic structure near the interface. Both types of effects for metal adlayers have been discussed in the context of the very successful d-band model proposed by Hammer, Nørskov and collaborators.[5] It has been theoretically shown that, for a wide variety of heteroepitaxial systems, the presence of the support leads to a modification of the d-band width of the adlayer, and in turn influences the average energy of the d-band, which rigidly shifts to maintain a constant filling.[6]

The effect of strain on the bandwidth is simple to understand: when the lattice expands parallel to the surface (tensile stress) the overlap between the d orbitals on neighboring atoms within the adlayer becomes smaller, which leads to less band dispersion and narrower bandwidth. Conversely, lattice contraction due to lateral compressive strain leads to wider bands. There has been abundant discussion of the strain effect in the theoretical literature since density functional theory (DFT) calculations by Mavrikakis et al. showed that the adsorption energies of atomic oxygen and molecular CO correlated with the shift of the d-band center produced by strain on the Ru(0001) surface, and successfully explained it by the bandwidth mechanism.[7] Experimentally, it has been observed that the adsorption behavior and the catalytic activity for

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formic acid electrooxidation of a palladium monolayer supported on various other metal surfaces, vary systematically with lateral compression or expansion as predicted by the d-band width/shift model.[8]

On the other hand, the precise nature of ligand effects for metal adlayers is slightly more elusive, probably because strain and ligand effects are very difficult to separate in practice. In order to isolate the ligand effects, Kitchin *et al.* performed a DFT study of unstrained Pt adlayers on (strained) metallic supports, and found that the d-band width/shift model can still be used to explain the modification of the electronic structure of the adlayer by the support.[9] The proposed mechanism is that the electronic interactions between the Pt adatoms and the subsurface metal atoms modify the matrix elements between the corresponding d-orbitals, leading to a change in the bandwidth. They pointed out that, within a tight-binding formalism, the bandwidth is proportional to the matrix elements between the d-orbitals, which depend both on the nature of the two metals and the interatomic separations. In the context of metal adlayers on metal supports, these matrix elements are expected to characterize the "strength" of the interaction between the adlayer and the support.

We will argue here that, at least for the particular system under study, the direct interaction between the adlayers and the support can be more simply described as charge transfer. Surprisingly, the role of charge transfer has been widely neglected in the literature on bimetallic systems, despite the fact that charge transfer should always be expected at the interface of metals with different workfunctions. The surface with the higher workfunction should receive electrons at the interface, which can be explained from the alignment of the band structure of the two separate metals with respect to the vacuum reference level: the Fermi level of the higher-workfunction metal will lie lower than that of the other, and therefore electronic equilibrium

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requires electron transfer to the metal with the higher workfunction, until the created interface dipole prevents further charge transfer.[10] The main reason why the role of charge transfer has been overlooked in this context is probably the success of the *d*-band model in explaining the electronic properties of metal adlayers, since the model assumes a constant filling of (and therefore no charge transfer to or from) the adlayer *d*-band. Another reason is some conflicting predictions made by simple charge transfer models about the core level shifts observed in experiment, as we will discuss below.

In order to focus on the direct support-adlayer interactions and exclude strain, we have studied an heteroepitaxial system where the lattice parameter of the adlayer is practically the same as that of the support: the Pd / Re(0001) system. Furthermore, by considering Pd adsorption beyond the single monolayer (ML), we can also investigate as a reference the electronic properties of consecutive layers where there is no direct interaction with the support at all. In recent experimental work from our group, Etman *et al*. fully characterized the systems formed by 1-4 ML of Pd on Re(0001), using quantitative low energy electron diffraction (LEED-IV), scanning tunneling microscopy (STM) and X-Ray photoelectron spectroscopy (XPS).[11] The LEED experiment identified the stacking sequence of the Pd layers. If the Re stacking of (0001) planes is denoted as ABAB (the *hcp* sequence), then the first layer of Pd continues the *hcp* sequence, so the deposited monolayer (1ML) can be denoted as ABABa. However, consecutive layers of Pd stack follow the *fcc* sequence, leading to the ABABac structure for 2ML, ABABacb for 3ML, and ABABacba for 4ML (**Figure 1**). The XPS spectrum in that study was measured using an unmonochromated X-ray source, which offered low resolution compared with synchrotron radiation. Therefore only one broad peak was found, which shifted systematically to lower binding energies as more Pd was deposited, until a point (between 2 and 3 ML deposition) from

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where the position of the peak remained constant. A previous study of the same system by Mun *et al.*[12] reported high-resolution XPS spectra using synchrotron radiation, where a separate peak with higher core-level binding energy could be resolved and assigned to the interface Pd layer, on the basis of its attenuation upon increasing Pd deposition. In order to resolve the apparent contradiction between higher binding energies of Pd core levels at the interface (which would be typically interpreted as electron charge depletion) and a measured lowering of the valence band center of these atoms away from the Femi level (which indicates electron gain), these authors invoked a charge redistribution picture from the theoretical work by Wu and Freeman,[13] according to which, the interaction between Pd and Re atoms at the interface results in *i*) charge accumulation in the interfacial region on top of the Re atoms and *ii*) charge depletion from both Pd and Re atoms. Here we will provide a different picture that disputes both the charge transfer model presented in Ref. 13 and its interpretation in Ref. 12. We will show how a simple charge transfer model can explain the experimental observations of the behavior of the core and valence levels in the Pd / Re(0001) system.
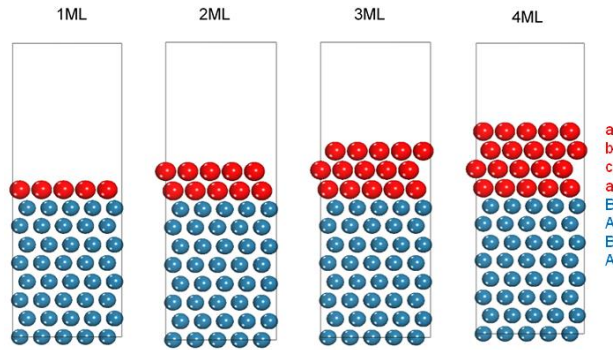

Figure 1. Schematic representation of stacked Pd / Re(0001) system. Red and blue balls correspond to Pd and Re atoms respectively. The stacking sequence shown here corresponds to the lowest-energy configuration in each case.

2. METHODOLOGY

Periodic DFT calculations were performed with the VASP program[14,15] using the generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.[16] The projected augmented wave (PAW) method[17,18] was used to describe the interaction between the valence electrons and the core. The number of plane waves was determined by a kinetic energy cutoff of 327 eV (set at 30% above the default value from PAW potentials in order to minimize Pulay errors).[19]

The Re(0001) surface was modelled with a periodic slab consisting of 8 layers, and a vacuum space of 20 Å. Only the four uppermost Re layers were fully relaxed, while the four bottom layers were fixed in the bulk positions (this procedure is often found to accelerate the convergence of calculated surface properties with respect to the thickness of the simulation slab[20,21]). Of course, the positions of the deposited Pd-layers were also allowed to fully relax. In order to compensate for the use of an asymmetric slab, all simulations included a dipole correction as implemented in VASP, based on a method proposed by Makov and Payne.[22]

Monkhorst-Pack grids[23] with a maximum separation of 0.15 Å^{-1} between k-points were used for sampling the Brillouin-zone. This grid density, which was checked with respect to convergence of the Re bulk total energy, corresponds to a 18×18×1 grid for the reciprocal space of the slab model. Ionic positions were relaxed using a conjugated gradient algorithm until the forces on atoms were all than 0.01 eVÅ^{-1}.

For bulk Re, the calculated unit cell parameters are a = 2.770 Å and c = 4.475 Å, which compare well with experimental values a_{exp} = 2.761 Å and c_{exp} = 4.458 Å (deviations of +0.3% and +0.4%). For bulk Pd, the calculated unit cell parameter is a = 3.935 Å, which is reasonable compared with the experimental value a_{exp} = 3.890 Å (deviation of +1.2%).[24] In both cases, the

positive deviations are as expected from the well-known GGA overestimation of metal lattice parameters.[25] The corresponding surface lattice parameters for Re(0001) (2.770 Å) and Pd(111) (2.782 Å) are thus very similar, giving only a very small compressive strain (-0.4%). Using experimental surface cell parameters (2.761 Å for Re(0001) and 2.751 Å for Pd(111)), the strain is actually positive (tensile) but also very small: +0.4%. We will show below that this small discrepancy with experiment does not affect the agreement between theory and experiment in terms of the electronic structure of the films, confirming that the effect of strain is negligible for this interface.

The formation energy (per surface site) of the interface with n Pd layers was calculated as:

$$\Delta E_\mathrm{f} = E_\mathrm{Pd/Re} - (E_\mathrm{Re} + nE_\mathrm{Pd}) \tag{1}$$

where $E_\mathrm{Pd/Re}$ represents the energy of the optimized Pd-Re system, E_Re corresponds to the energy of the relaxed clean Re surface, and E_Pd denotes the energy per atom of Pd bulk. The transferred charge density $\Delta\rho$ was calculated by subtracting, from the charge density of the Pd-Re system, the sum of the charge densities of the clean Re surface and Pd layers (calculated at the same geometry which they have at the interface):

$$\Delta\rho = \rho_\mathrm{Pd/Re} - (\rho_\mathrm{Re} + \rho_\mathrm{Pd}) \tag{2}$$

Effective atomic charges were computed using the Bader methodology,[26] where the three-dimensional space is partitioned into basins, (typically) belonging to individual atoms, delimited by surfaces through which the flux of the density gradient is zero. For our Bader analysis we used the implementation by Henkelman *et al.*[27–29]

We calculated core-level shifts in the so-called final-state approximation,[30] computed as total energy differences between two separate calculations.[31] The first one is a standard DFT

calculation performed on the fully relaxed system. In the second calculation, one electron from the chosen core level of a specific atom is excited to the lowest conduction band state, allowing only the valence electronic structure to be relaxed at fixed atomic configuration. The total energy difference between the two calculations is an estimate of the core-level binding energy, without taking into account the effect of core-electron screening (although screening by valence electrons is included). The method is not able to yield absolute values for the core level binding energies,[31] and in any case, the calculation of such absolute values from DFT is fundamentally problematic.[32] Thus one must consider core level *shifts* (E_{CLS}), which can be defined as the variation in binding energy of specific core-electrons (E_{CL}) of atoms compared to reference atoms (E_{CL}^{ref}):

$$E_{CLS} = E_{CL} - E_{CL}^{ref} \tag{3}$$

The reference system in our study, whenever we report core level shifts, was taken as Pd bulk. However, we are mainly interested in the relative shifts of the core levels of Pd atoms in different layers, therefore the selection of reference is systematically unimportant.

   Finally, we have calculated valence *d*-band properties as follows: the position of the center (E_d) is obtained from the first moment of the *d*-projected density of states ($g_d(E)$) with respect to the Fermi level (E_F):

$$E_d - E_F = \frac{\int_{-\infty}^{\infty} g_d(E)(E - E_F) dE}{\int_{-\infty}^{\infty} g_d(E) dE}, \tag{4}$$

the root-mean-squared width W_d of the *d*-band is obtained from the second moment of the DOS with respect to the band center:

$$W_d^2 = \frac{\int_{-\infty}^{\infty} g_d(E)(E - E_d)^2 dE}{\int_{-\infty}^{\infty} g_d(E) dE}, \tag{5}$$

and the *d*-band filling is calculated as:

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$$f_{\mathrm{d}} = \frac{\int_{-\infty}^{E_{\mathrm{F}}} g_{\mathrm{d}}(E)\,\mathrm{d}E}{\int_{-\infty}^{\infty} g_{\mathrm{d}}(E)\,\mathrm{d}E} \times 100\%. \tag{6}$$

3.   RESULTS AND DISCUSSION

3.1   **Interface geometry and stability.** The calculated formation energies for the different possible stacking sequences are summarized in **Table 1**. There is a perfect match between the lowest-energy stacking configuration and the one with the lowest Pendry factor (R_{p}), which corresponds to the best structural fit to the LEED data in Ref. 11. Therefore our theoretical result confirms the preferred growth suggested by experiment, in which the first layer adopts an *hcp* pseudomorphic structure ABABa; the second layer introduces a stacking fault to give a *fcc*-like termination ABABac, with subsequent layers growing in an *fcc* pattern. The fact that the experimental configuration corresponds in each case to the one with the lowest energy suggests that the stacking sequence of the Pd films is thermodynamically controlled during growth.

Table 1. Formation energies for the different possible stacking sequences. ABAB represents the *hcp* sequence of Re layers. Lowercase letters indicate the relative stacking of the Pd layers. LEED results are from Ref. 11.

Underlined/bold entries represent the lowest DFT energy or best experimental fit.

No. of ML	Stacking	ΔE_{f} (eV)	LEED R_{p} factor
1	**ABABa**	**-0.588**	**0.218**
	ABABc	-0.527	0.465
2	ABABab	-0.698	0.351
	ABABac	**-0.722**	**0.211**

	ABABca	-0.593	0.268
	ABABcb	-0.570	0.386
	ABABaba	-0.597	0.419
	ABABabc	-0.617	0.284
	ABABaca	-0.603	0.404
3	**ABABacb**	**-0.621**	**0.248**
	ABABcab	-0.521	0.275
	ABABcac	-0.509	0.396
	ABABcba	-0.496	0.303
	ABABcbc	-0.479	0.420
	ABABacab	-0.607	0.288
	ABABacac	-0.587	0.475
4	**ABABacba**	**-0.630**	**0.209**
	ABABacbc	-0.612	0.446

In **Figure 2** we plot the formation energy of the preferred stacking configurations at each composition against the number of deposited layers. The negative values indicate that the deposition is an energetically favorable process with respect to Pd atoms in the bulk and the free Re surface. Our calculations predict a shallow minimum of the interface formation energy at 2ML Pd. From the shape (convex hull) of the variation of the formation energy with the number of deposited layers, we conclude that the homogeneous 3ML composition is thermodynamically unstable (by 55 meV per surface unit cell) with respect to separation into islands of 2ML and 4ML, if we ignore border contributions. However such separation is not observed in the

experiment, where the 3ML system was found to be homogeneous and fit well a model with ABABacb sequence. Therefore, our results suggest that the separation of the homogeneous system into a heterogeneous system with islands of different thicknesses might be kinetically limited under the conditions of these experiments, even when the stacking follows the thermodynamically preferred sequence.
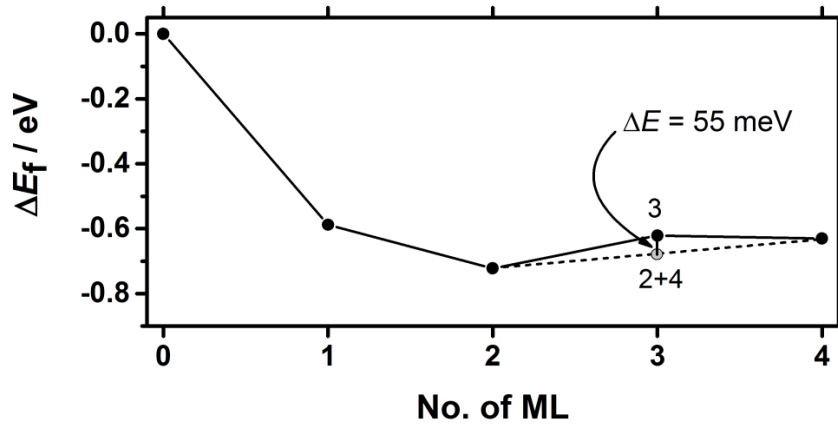

Figure 2. Interface formation energy (energy relative to free Re surface and Pd bulk) as a function of Pd coverage. Straight lines joining the points are a guide to the eye.

The optimized interlayer distances for the slabs are summarized in **Table 2**. The DFT values of the interlayer distances are also consistent with LEED measurements, with good quantitative agreement within the experimental error in most cases. The small contraction of the Pd-Re interface, with respect to Pd-Pd distances, could be a consequence of charge transfer at the interface, which will be discussed later.

Table 2. Calculated interlayer distances in comparison with experiment.[11] The italicized/bold entries correspond to the Re-Pd interface.

Interlayer separation	1ML		2ML		3ML		4ML	
	DFT	Exp.	DFT	Exp.	DFT	Exp.	DFT	Exp.
d_{12} (Å)	*2.23*	*2.20±0.05*	2.32	2.30±0.04	2.31	2.34±0.04	2.31	2.30±0.03
d_{23} (Å)	2.16	2.18±0.03	*2.20*	*2.23±0.03*	2.33	2.29±0.04	2.30	2.28±0.03
d_{34} (Å)	2.29	2.25±0.04	2.17	2.19±0.07	*2.22*	*2.28±0.07*	2.34	2.30±0.05
d_{45} (Å)	2.21	2.23±0.06	2.29	2.30±0.07	2.17	2.17±0.13	*2.22*	*2.30±0.06*

3.2 **Charge transfer at the interface.** In order to understand the nature of the interaction between the substrate and the Pd thin-films, as well as the electronic structure presented below, we now discuss the occurrence and magnitude of the charge transfer at the interface. **Figure 3** shows a cross-section plot of the transferred charge density $\Delta\rho$, as given by equation (2), for the case of 1 ML Pd on Re(0001). There is a clear charge transfer of electrons from Re to Pd. The transferred charge is polarized in such a way that it is mostly located "below", *i.e.* at the side pointing towards the Re support. We have checked that this asymmetry of the transferred charge distribution is not a consequence of the choice of the projection plane.

Therefore, we disagree here with the conclusion from the theoretical work of Wu and Freeman[13] on the 1ML Pd / Re(0001) system, where they state that the interaction between Pd and Re results in charge accumulation in the interfacial region, with electron depletion from *both* Pd and Re atoms. Our conclusion that Pd is instead a net receiver of negative charge is supported

by the Bader analysis of the DFT charge density (**Table 3**), which shows that in the case of 1 ML deposition, the Pd atoms adopt an effective charge of -0.18 e, while the top Re atoms adopt a positive charge of +0.15 e, with an additional small amount of positive charge (+0.03 e) in the second Re layer. In the case of multi-layer Pd deposition, the Bader analysis shows that the Pd layer at the interface always contains most of the negative charge, although in the case of 2ML deposition the negative charge at the second Pd layer is also significant (-0.07 e). The top Re layer accounts for most of the positive charge in all cases, and the total amount of transferred charge is practically independent on the number of Pd layers deposited.

The charge transfer direction from Re to Pd at the interface is as expected on the basis of the lower workfunction of Re compared to Pd: our calculated workfunction values for the Re(0001) and Pd(111) surfaces are 4.91 eV and 5.27 eV, respectively (values of 4.72 eV and 5.22 eV are reported from experiment for polycrystalline Re and Pd).[33] As explained above, the surface with the higher workfunction is expected to receive electrons at the interface, which can be explained from the alignment of the electron bands of the two separate metals with respect to the vacuum reference level.[10]
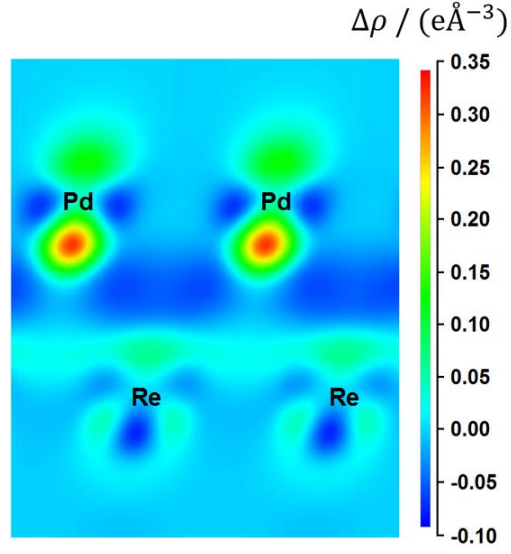
Figure 3. Contour plot of the transferred charge density for the system with 1 ML Pd on Re(0001). The plane of the figure was chosen in such a way that the cross-section contains both Pd atoms and Re atoms at the interface.

Table 3. Bader analysis for the clean Re (0001) and its interfaces with Pd thin films of different thicknesses.

Atoms	clean	1ML	2ML	3ML	4ML
Pd	-	-	-	-	-0.03
Pd	-	-	-	-0.03	0.03
Pd	-	-	-0.07	-0.01	-0.04
Pd	-	-0.18	-0.10	-0.12	-0.12
Re	-0.07	0.15	0.14	0.14	0.14
Re	0.06	0.03	0.03	0.03	0.03
Re	0.00	0.00	0.00	0.00	0.00
Re	0.01	0.00	0.00	0.00	0.00

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3.3   **Core-level shifts and simulated XPS spectra.** We have theoretically simulated the XPS

spectra by calculating final-state Pd $3d$ core-level shifts using DFT. Gaussian curves were used

for broadening the contribution from each layer; their intensities are given by an exponential

attenuation with the distance to the surface afforded for the inelastic mean free paths, while their

widths are determined by the resolution of the experiment being simulated (**Figure 4a**). The

solid curves in **Figure 4a** correspond to the simulation of laboratory-based XPS data such as that

shown in **Figure 4b**, which is reproduced here from Ref. 11. The dashed curves correspond to

the simulation of high-resolution synchrotron XPS, where separate peaks are resolved; this can

be compared with the experimental results presented in Ref. 12.

The basic features of both low-resolution and high-resolution XPS experiments are well

reproduced by our DFT-simulated XPS spectra. The low-resolution peaks initially shift to lower

binding energies (BE) with increasing Pd coverage, and then remain constant after 2-3 ML

deposition. High-resolution signals split into two peaks; the one with the higher BE decreases its

relative intensity with increasing Pd coverage.

The XPS simulation allows us to unambiguously determine the origin of the different

contributions to the spectrum. In the high-resolution spectrum, we confirm the assignment of the

higher BE peak to the contribution from Pd atoms at the interface, as originally proposed by Mun

et al.[12] The lowest BE contributions arise from the surface Pd atoms, which are similar to the BE

from the bulk-like layers in between. Even the synchrotron-radiation XPS cannot clearly resolve

these two types of contributions (surface and "bulk" of the film), and therefore they visually

appear as a single peak (figure 1 in Ref. 12), although the authors mention that fitting the

spectrum does indicate the presence of a "surface" peak shifted by 0.3 eV with respect to bulk

peaks. In our calculations for the 4ML system, we find that the binding energy difference

between the surface layer and the average of the two bulk-like layers is 0.26 eV, in good agreement with their fitting result.

The higher BE of the core levels of the interface Pd atoms has to be reconciled with our previous conclusion about the transferred charge localization on these atoms. In the analysis of core level shifts, a higher BE is often associated with a more positive ion, which is rationalized by the stronger Coulomb attraction between a more positive ion and the electron being ejected. However, here we are finding a shift to higher BE for the more negative Pd ion at the interface. In fact, the commonly used association between shift to higher BE and electron depletion, which our results contravene, is now known to be generally inadequate, in particular for interpreting core level shift in surface adlayers.[34] The correct explanation for the sign of the core level shifts will be discussed below, on the basis of the behavior of the valence electronic structure of this system.
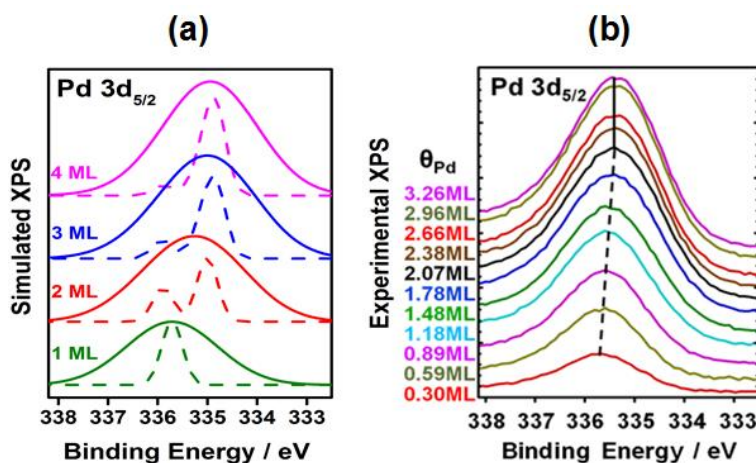

Figure 4. XPS spectra as a function of Pd coverage on the Re (0001) surface: (a) DFT simulation, where solid and dashed lines represent low-resolution and high-resolution spectra, respectively; (b) Low-resolution XPS obtained with photon energy of 1486.6 eV, reproduced from Ref. 11. The high resolution simulation is based upon the experimental conditions of Ref. 12 where a photon energy of 450 eV was employed.

3.4. **Valence electron density of states and *d*-band centers.** We have calculated the electronic density of states (DOS) projected on the 4*d* valence orbitals of Pd atoms, layer by layer. The results for the surface and interface layers are shown in **Figure 5a**. It is clear that the *d*-band center for the interface Pd atoms (dashed lines) is shifting to lower values, away from the Fermi level, compared to the *d*-band center of surface Pd atoms. On the other hand, **Figure 5b** shows that for all Pd atoms in the films, a shift in the 4*d* valence level corresponds to a shift in the same direction and of similar value as that of the 3*d* core level. This remains true regardless of whether we use initial-state or final-states core-level shifts (correlation $R^2>0.95$ in both cases). The gradients of the linear fit lines are 1.09 (initial-state shifts) and 1.16 (final-state shifts); the proximity to 1 indicates that we have nearly rigid shifts of the core and valence levels with respect to the Fermi level.
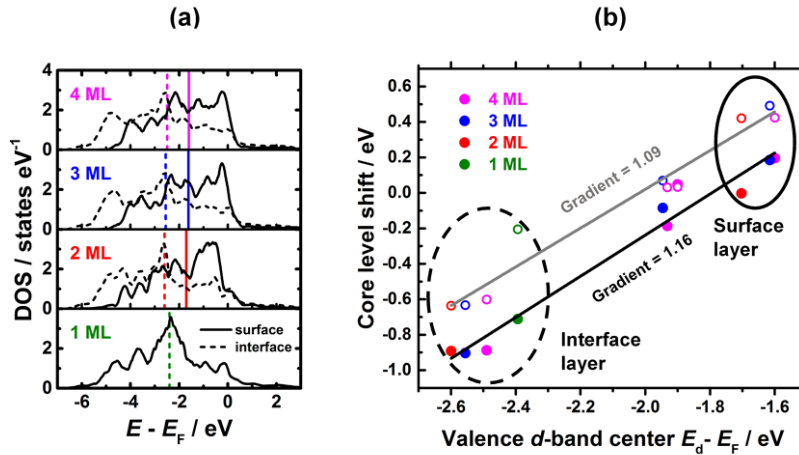

Figure 5. (a) Electronic density of states (DOS) projected on the Pd 4*d* orbitals of the surface (solid lines) and interface (dashed lines) atoms, with the corresponding *d*-band centers marked by vertical bars. (b) Correlation between Pd 3*d* core-level shifts and Pd 4*d* band centers. The initial-state and final-state shifts are shown with empty and filled circles, while the corresponding best-fit lines and their gradients are shown in gray and black, respectively.

The similarity between the results using initial-state and final-state shifts in **Figure 5b** implies that initial state effects dominate the binding energies. The shift of the core levels should be seen as a consequence of a change in the electronic structure of the valence, and therefore as an initial-state effect arising through the shift in the entire local potential at the sites. The correlation between core and valence level shifts of metal surfaces and adlayers has been discussed before by several authors.[34–37] This correlation is important from a practical point of view because it implies that XPS measurements of core level shifts carry value as experimental predictors of surface adsorption and reactivity behavior, in the same way as the *d*-band shifts are useful theoretical predictors of these properties. The XPS technique is well established and commonly used to characterize catalyst materials and hence this experimental descriptor constitutes a very practical choice, as was noted in an early study by Rodriguez and Goodman.[1]

However, what is more interesting from our results, and in contrast to previous work, is the discussion of the mechanism causing the valence *d*-band shift in the first place. In strained metallic adlayers, it is customary to explain this behavior via the "bandwidth mechanism", which we illustrate in **figure 6a**. In the presence of tensile strain, the metal atoms are laterally more separated in the adlayer, which leads to a decrease in the *d*-band width. If one assumes no charge transfer to the *d*-band, a narrowing of the (more than half-filled) band is necessarily accompanied by a shift upward of its center, towards the Fermi level, in order to preserve band filling. Conversely, in the presence of compressive strain, the width of *d*-band will increase and its center will shift down, away from the Fermi level.[4] Clearly, in our case this mechanism has to be rethought because a) the strain in the Pd adlayers on Re (0001) is negligible, and b) we have shown that there is significant charge transfer at the interface.

Table 4 shows that, for any given composition, all Pd layers have a similar degree of d-band filling (f_d), despite the differences in charge identified above using Bader analysis. Even for different compositions, the degree of band filling is very similar in all cases (between 90 and 93%), decreasing only slightly with the thickness of the layer. The reason why the charge transferred to the Pd layer at the interface is not going to states of d character is that the polarization of the transferred charge, which is illustrated in **Figure 3**, is not compatible with the symmetry of d orbitals. Instead, a hybrid of valence s and p orbitals is a more appropriate description, due to constructive interference between the mixing orbitals on one of the p lobes (the one pointing towards the interface) and destructive interference in the opposite one. The electron population decomposition analysis (integration of s, p, d - projected charges within PAW spheres) in Table 4 shows that, indeed, there is always significant increase in the s-p population of the interface Pd compared with the other layers. It should be noted here that the total charge differences obtained from integration within atomic spheres are similar to those identified using Bader analysis (defined for non-spherical atomic basins), which confirms that our conclusions about the presence and magnitude of charge transfer are valid regardless of the definition of the atomic regions.

Since the filling of the d-band is roughly constant for each composition, the inverse correlation between the valence d-band width and the d-band center shift, which is expected for strained systems, is also observed in our case (**Figure 7**). The relative displacement of the lines for different compositions is reflecting the slightly different band filling degrees. The inverse correlation between bandwidth and band center shift simply indicates a constant degree of d-band filling, regardless of whether the shift is induced by strain or by charge transfer to the s-p band. But whereas in the strain case the bandwidth change is a direct consequence of strain, and

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the center shift results from the bandwidth change, in our charge-transfer picture the bandwidth change is not driving the band center shift, but it is a consequence of it.

Table 4. Layer by layer d-band filling and electron population of the s, p and d valence bands as obtained from the integration of the projected densities (within PAW spheres) of states up to the Fermi level. The values corresponding to the interface Pd layer are highlighted with italics/bold font.

System	Pd layer (from top)	d-band filling f_d	Electron population		
			s	p	d
1ML	1	*93%*	*0.51*	*0.40*	*8.52*
2ML	1	93%	0.47	0.32	8.49
	2	*91%*	*0.51*	*0.54*	*8.45*
3ML	1	92%	0.45	0.32	8.49
	2	91%	0.47	0.43	8.46
	3	*90%*	*0.52*	*0.53*	*8.45*
4ML	1	91%	0.45	0.33	8.48
	2	90%	0.46	0.44	8.44
	3	90%	0.47	0.43	8.46
	4	*90%*	*0.52*	*0.53*	*8.45*

To illustrate the above point, the simplified scheme in **Figure 6b** shows the effect of charge transfer to s-p levels on the position and width of the d-band. The key here is that all valence (and also core) levels shift almost rigidly with changes of the site potential. Thus the filling of

the *s-p* band due to interface charge transfer is accompanied by a down shift of the *d*-band center with respect to the Fermi level. But since the filling of *d*-band center should remain constant, its width must increase to preserve the degree of filling.

Thus our analysis shows that the behavior of the *d*-band in the Pd unstrained adlayer can be simply explained by charge transfer from the Re support, which can be seen as analogous to the application of support-induced compressive strain (which does not exist in this case). One could also expect that charge transfer in the opposite direction, *i.e.* electron moving from the adlayer to the support (the obvious case to study here to exclude strain effects would be Re deposited on Pd(111)), is analogous to support-induced tensile stress.
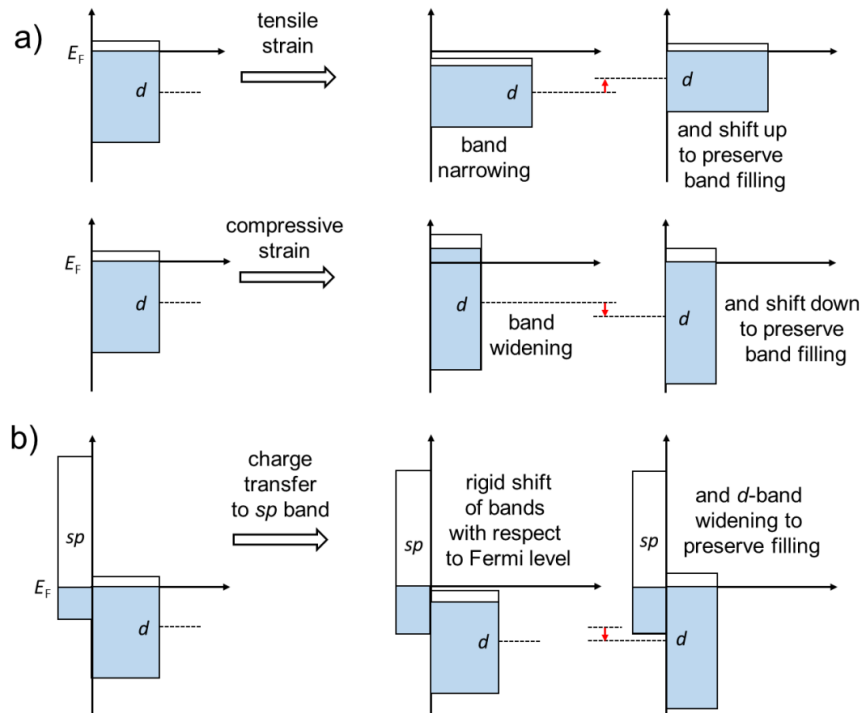

Figure 6. Origin of the valence *d*-band shift a) in the presence of tensile or compressive strain but absence of charge transfer, and b) when there is no strain but instead there is charge transfer to the adlayer *sp* valence levels, as in the case of Pd / Re(0001).

It is likely that even in the case of strained interfaces, small amounts of charge transfer will contribute to the behavior of the metal d-band through the mechanism proposed here, which calls for a reexamination of the role of charge transfer in other (strained or not) metallic films on metal supports. For example, we have briefly considered the case of only 1ML of Pd on Ru(0001), where a down-shift of core and valence levels has recently been described experimentally and theoretically.[37] In this case, there is significant compressive strain (-1.6% using experimental cell parameters). While the effect of strain can explain the direction of the shift, it is likely that its magnitude is also affected by charge transfer, as these two metals exhibit different workfunctions (we have calculated 4.96 eV for Ru(0001), which is similar to that of Re(0001) and well below the value of 5.27 eV computed for Pd(111)). The Bader analysis in this case confirms that there is charge transfer to the Pd adlayer, of ~0.11 electrons per atom. Therefore, the shift in the valence and core levels in that case probably has contributions from both strain and charge transfer.
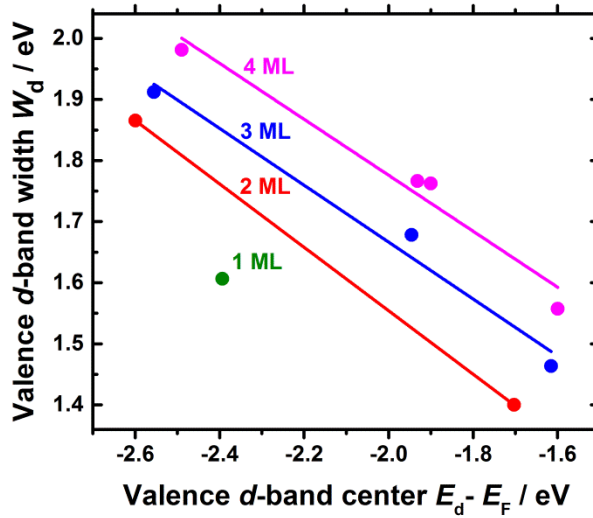

Figure 7. Correlation between the width of the Pd valence d-band and the position of its center with respect to the Fermi level.

4. CONCLUSIONS

Our theoretical study of few-layer Pd films deposited on the Re(0001) surface has led to the following conclusions:

a) The stacking sequence observed experimentally, whereby the first layer of palladium continues the *hcp* sequence of the rhenium stacking, while consecutive layers adopt the *fcc* sequence expected for palladium, is the lowest-energy one, implying that the layer-by-layer growth is mainly thermodynamically controlled. However, in the case of deposition of 3ML Pd, the thermodynamically preferred separation into islands of 2ML- and 4ML-depth predicted by calculations has not been observed in experiment, suggesting that this rearrangement process might be kinetically limited.

b) There is a significant amount of charge transfer from Re to Pd, mainly localized at the interface layers. The charge transferred to Pd is polarized in such a way that it is "pointing" towards the Re support. That means that the transferred charge cannot be projected onto Pd *d* states, and its better described as being transferred to hybrid *sp* states in the valence.

c) The charge transfer from Re to the interface Pd adlayer produces a rigid shift to more negative energies of the electronic band centers on this Pd layer, compared to those at the next layers. But because the valence *d*-band preserves its degree of filling in all cases, its width for the interface Pd layer has to increase. In general, an inverse correlation is then observed between *d*-band center shifts and bandwidths.

d) The shift in the valence states is accompanied by an almost rigid shift in the core states. Therefore the Pd $3d$ states at the interface layer have higher binding energies that those from consecutive layers. The change in the experimental XPS as a function of the number of deposited layers is well explained by a theoretical simulation of the XPS signal: there is a

gradual shift to lower binding energies as the interface layer is "buried" by further Pd deposition.

e) The charge transfer model can therefore explain in a simple way the effect of the support on the electronic structure of core and valence levels in this unstrained system. We have shown that it is possible to establish an analogy between the application of a support-induced compressive (tensile) strain and the charge transfer to (from) the adlayer. While in the present case of Pd/Re(0001) the strain is very small and the electronic structure changes are determined by charge transfer effects, in general cases both strain and charge-transfer could contribute to the observed behavior. Our results and analysis then call for a reexamination of the role of charge transfer in the electronic behavior of metal adlayers on metal supports.

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TOC Graphic: