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Effect of hydrogen on the surface relaxation of Pd(100), Rh(100), and Ag(100)

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Hydrogen induced surface relaxations of Pd(100), Rh(100), and Ag(100) have been studied by density functional theory calculations. We find that the first interlayer spacings of Pd(100) and Rh(100) expand almost linearly with hydrogen coverage. This result is used to estimate the amount of remaining hydrogen atoms on the surface samples investigated in previous low-energy electron diffraction studies, unusually large top-layer expansions of which have been suggested due to hydrogen contamination. The estimated H coverages of 0.5–1.1 ML, unexpectedly high for the samples claimed as clean, indicates that Pd(100) and Rh(100) are extremely susceptible to H contamination, requiring a more careful surface cleaning process. Hydrogen adsorption could result in a significantly large top-layer expansion in Ag(100), but such H effect is not realized in experiment since a dissociative adsorption of H_2 on Ag(100) is energetically improbable.

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I. INTRODUCTION

The surface relaxation of Pd(100) has long been a subject of disputes. Low-energy electron diffraction (LEED) studies[1–3] reported that the first interlayer spacing (d_{12}) of Pd(100) is expanded by 2.5%–4.6% relative to the bulk value. This top-layer expansion, exceptional in a sense that most of 4*d* transition-metal surfaces show an inward relaxation,[4] is not supported by theoretical calculations[4–8] which predicted a contraction of about 1%. As a possible origin of the unusual surface relaxation of Pd(100), hydrogen contamination was proposed early by Quinn *et al.*[2] It is expected that residual hydrogen gas molecules dissociate easily on the reactive Pd(100) surface, and the resulting H-Pd interaction may rather weaken the Pd-Pd backbonding, thereby expanding the first interlayer spacing. This hydrogen issue is in line with the prediction of first-principles calculations[5,6] that Pd(100) undergoes a top-layer expansion of ~5% upon hydrogen adsorption of 1 ML (one H atom per 1×1 surface unit cell), but a conclusive experimental investigation for the extent of hydrogen contamination and its effect on the surface relaxation has been delayed due to the difficulty with detecting hydrogen and the possibility of incorporation of H into the Pd lattice.

Recently, in their LEED study of the H/Pd(100) surface, Kim *et al.*[9] demonstrated that (1) the Pd(100) surface with the surface hollow sites fully occupied by hydrogen shows a lattice expansion of $\Delta d_{12}=4.7\%$ in agreement with theoretical predictions[5,6] of $\Delta d_{12}=4.4\%-5.2\%$, (2) the sample prepared by heating above the hydrogen desorption temperature or by rapid cooling after quick thermal treatment to remove hydrogen shows almost no top-layer expansion, and (3) hydrogen readsorption from the residual gas atmosphere leads to an expansion in a range of $\Delta d_{12}=2\%-3\%$ as observed in previous LEED experiments.[1,2] This LEED study is considered to be sufficiently systematic to clarify the hydrogen origin of the unusual top-layer expansion of the Pd(100) surface, leading to a conclusion that the Pd(100) samples investigated in previous LEED studies[1–3] were not hydrogen free. A natural question is what amount of hydrogen atoms remain on the examined surface samples. A theoretical study of the relation between the top interlayer spacing and the H coverage (θ) will be useful in estimating the amount of remaining H atoms from the measured surface relaxations. It is also interesting to see how hydrogen contamination affects the relaxation of Rh(100) and Ag(100), the two neighboring 4*d* transition-metal surfaces of Pd(100).

In this paper we quantify the effect of hydrogen on the surface relaxation of Pd(100) using density-functional theory (DFT) calculations. We determine the top-layer relaxation of Pd(100) as a function of H coverage. The resulting Δd_{12} values, increasing almost linearly with coverage, are used to predict the amount of hydrogen atoms remaining on the Pd(100) samples used in previous LEED experiments. We also extend our study to Rh(100), another surface exhibiting a controversial expansion of the first interlayer spacing,[10–15] and Ag(100), a neighbor of Pd(100) but showing no evidence of top-layer expansion.

II. METHOD

We perform density functional theory calculations using the Vienna *ab initio* simulation package (VASP).[16] Exchange and correlation is treated by the generalized gradient approximation (GGA) of Perdew-Wang '91 (Ref. 17), and ionic potentials are represented by ultrasoft pseudopotentials.[18] We simulate metal surfaces using a repeated slab geometry. Each slab consists of eight layers of metal atoms, and the vacuum separation is equivalent to five atomic layers. Hydrogen atoms are adsorbed on both sides of the slab. In the course of structural relaxation four innermost layers are held at bulk positions. The used theoretical bulk lattice constant is 3.85 Å for Rh, 3.96 Å for Pd, and 4.17 Å for Ag. We use a plane-wave basis with a kinetic energy cutoff of 15.1 Ry for Rh, 14.7 Ry for Pd, and 14.7 Ry for Ag. Brillouin-zone integrations are done with a $(12\times12\times1)$ *k* point mesh for the (1×1) surface unit cell and with equivalent *k* meshes for the lower-coverage (2×2) and (3×3) cells. We carry out a number of electronic steps until the total energy difference is within 1×10^{-4} eV and a number of ionic steps until the

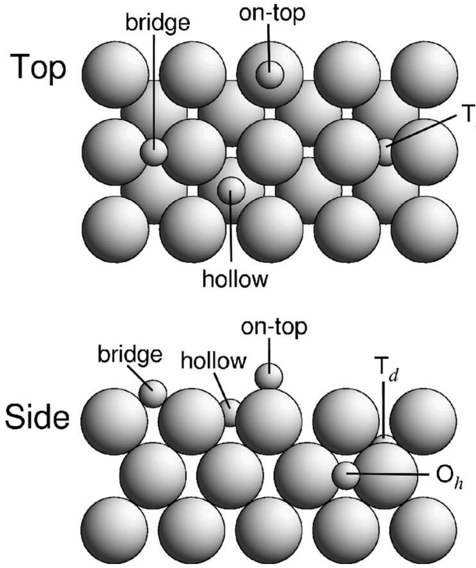

FIG. 1. Surface geometry of Pd(100). Surface and subsurface hydrogen adsorption sites are indicated.

residual force components of unconstrained atoms are within 1×10^{-2} eV/Å. The used parameters result in sufficiently converged energetics and structural properties. The calculated adsorption-energy differences and Δd_{12} were found to converge within 0.01 eV and 0.3%, respectively.

III. RESULTS

Figure 1 shows the adsorption sites on Pd(100) considered here, the on-top, bridge, and hollow sites for surface adsorption and the tetrahedral (T_d) and octahedral (O_h) sites for subsurface adsorption. It has been reported that the surface saturation coverage of hydrogen on Pd(100) is about 1 ML,[19–22] the hollow site is the most stable at the saturation coverage,[5,6,9,21] and after saturation hydrogen penetrates into subsurface or diffuses into bulk.[5,22,23] We first investigate as a reference system the Pd(100) surface with 1 ML hydrogen saturating the hollow sites. Table I shows the calculated Δd_{12} and Δd_{23} in comparison with previous theories and experiments. The H-induced large expansion of $\Delta d_{12}=4.8\%$ agrees with those of previous theories and a recent LEED experiment by Kim *et al.*[9] In the clean Pd(100) surface, however, the calculated small contractions of d_{12} differ from experimental large expansions except the result of Kim *et al.*[9] In both clean and H-covered Pd(100) surfaces, the magnitudes of Δd_{23} are small compared to Δd_{12}, and their discrepancy between experiment and theory is negligible.

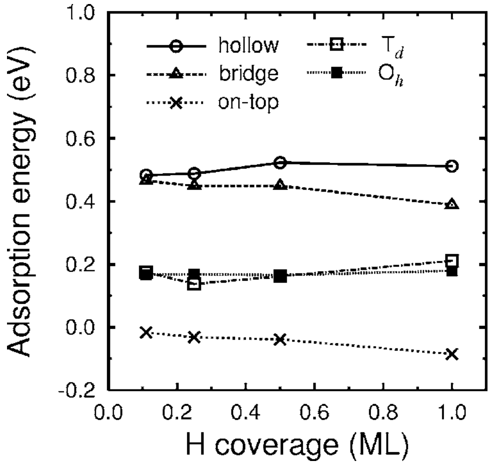

FIG. 2. Adsorption energetics for H/Pd(100) at different coverages.

We next consider the coverage dependence of the hydrogen effect on Pd(100). Figure 2 shows the adsorption energetics at different coverages up to 1 ML. The adsorption energy is defined as the energy gain per H atom relative to a

TABLE I. Surface relaxations of the clean and H-covered Pd(100) surfaces. In the H/Pd(100) system, hydrogen atoms of 1 ML are adsorbed on the hollow site. Δd_{ij} represents the percent (%) change of the interlayer spacings. z_H (Å) represents the vertical height of hydrogen atoms from the first Pd layer.

	Clean Pd(100)		H/Pd(100)		
Methods	Δd_{12}	Δd_{23}	Δd_{12}	Δd_{23}	z_H
Present theory	−1.3	−0.2	+4.8	+0.6	+0.20
DFT-FLMTO[a]	−0.6		+5.2		+0.11
DFT-USPP [b]	−1.0	+0.1	+4.4	+0.2	+0.20
LEED[c]	+2.5±2.5				
LEED[d]	+3.0±1.5	−1.0±1.5			
LEED[e]	+4.6±1.5	+0.3±0.5			
LEED[f]	+0.2±1.4	−0.7±1.3	+4.7±1.1	+0.0±0.9	$+0.20^{+0.43}_{-0.22}$

[a] Reference 5.
[b] Reference 6.
[c] Reference 1.
[d] Reference 2.
[e] Reference 3.
[f] Reference 9.

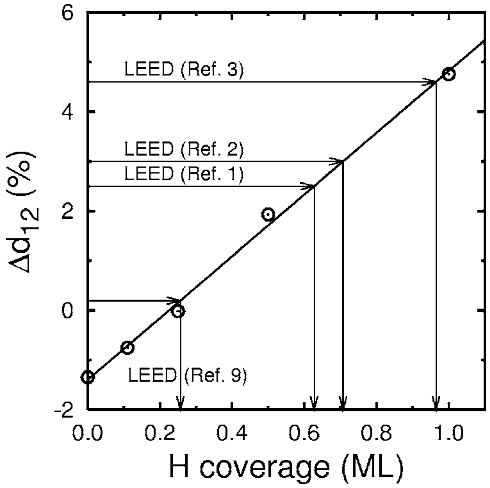

FIG. 3. Top-layer relaxation Δd_{12} of H/Pd(100) as a function of coverage. Hydrogen is assumed to adsorb on the hollow site. Circles represent the calculated points which fit to a linear curve. The amount of remaining hydrogen atoms in previous LEED samples are interpolated from the linear relation.

free H_2 molecule. The hollow site is found to be the most stable at any coverages with nearly constant adsorption energies of about 0.5 eV, in agreement with previous studies.[5,24] The bridge site appears less stable by 0.12 eV than the hollow site at $\theta=1$ ML, but the energy difference becomes negligible as 0.02 eV at $\theta=0.11$ ML, indicating that the adsorption on bridge sites is also probable at very low coverages. Subsurface O_h and T_d sites are far less stable with adsorption energies of about 0.2 eV than the surface hollow or bridge sites, indicating that subsurface hydrogen penetrations seem unlikely at coverages below 1 ML.

We examine the surface structural changes upon H adsorption. Figure 3 shows Δd_{12} at different coverages of the Pd(100) surface with H on the hollow site. For the calculation of Δd_{12}, we defined the height of a layer as the average height of all atoms in the layer, since the surface layers are rumpled by hydrogen adsorption, especially at low coverages. For example, at $\theta=0.11$ ML [i.e., one H atom per (3×3) unit cell], the hydrogen atom adsorbed on a hollow site slightly attracts its four nearest Pd atoms, the lateral displacements from their bulk positions are ~0.01 Å, and the difference in vertical displacement between the four nearest Pd atoms and the other five Pd atoms is ~0.02 Å. This small rumpling even decreases with H coverage and disappears at $\theta=1$ ML by symmetry. We find in Fig. 3 that Δd_{12} increases almost linearly with coverage. This linearity was mentioned before by Wilke *et al.*[5] although they showed only the results at $\theta=0$ and 1 ML. Given that hydrogen contamination is the origin of the unusual top-layer expansion reported in LEED experiments, this linear dependence of Δd_{12} on H coverage provides a basis to estimate the amount of surface hydrogen on Pd(100). As indicated in Fig. 3, the hydrogen coverages of the Pd(100) samples used in previous LEED experiments[1–3,9] are estimated by interpolation as $\theta \sim 0.26$, 0.63, 0.71, and 0.97 ML from the measurements of $\Delta d_{12} \sim 0.2\%$, 2.5%, 3.0%, and 4.6%, respectively. The prediction of such high coverages of 0.63–0.97 ML for early LEED samples[1–3] is rather surprising in view that the samples were claimed as clean. The (1×1) LEED patterns observed at such H-contaminated Pd(100) surfaces can be attributed to the fact that hydrogen is a very weak scatterer for electrons and hardly affects the substrate structure as indicated by the calculated small rumpling. Our prediction of 0.26 ML for the surface sample of Kim *et al.*[9] indicates that hydrogen was not removed completely even in their careful sample treatment.

In their surface x-ray diffraction (SXRD) study, Kim *et al.*[9] reported a large expansion of $\Delta d_{12}=5.8\% \pm 2.6\%$ and $\Delta d_{23}=2.4\% \pm 2.8\%$ for a Pd(100) surface prepared by applying so long cooling and data collection time of 40 hours. Considering the extremely long sample preparation time and a relatively large expansion of d_{23}, subsurface hydrogen penetration was speculated by the authors. To check such a possibility, we examine the energetical and structural properties of subsurface H adsorption at coverages beyond the saturation coverage. The results obtained for $\theta=1.25$ and 1.5 ML are shown in Table II. In both coverages, additional hydrogen atoms prefer the subsurface O_h site, and the hydrogen penetration into O_h sites leads to large expansions of the first two interlayer spacings in agreement with the speculation of Kim *et al.*[9] If time for data collection after the annealing is long enough, the Pd(100) surface is likely to be covered by residual hydrogen atoms above 1 ML. It is noticeable that the result obtained at $\theta=1.25$ ML is compared well with the structures measured by SXRD experiment.

Rh is a nearest neighbor of Pd in the Periodic Table, and the surface relaxation of Rh(100) is also exceptional. While LEED[10–14] and photoelectron diffraction (PED)[15] studies reported small top-layer relaxations of $\Delta d_{12}=-2\%-+1\%$, the-

TABLE II. Adsorption properties of H on Pd(100) at $\theta=1.25$ and 1.5 ML. We assume that hydrogen atoms of 1 ML preoccupy the surface hollow site and additional hydrogen atoms penetrate into subsurface sites. Adsorption energy E_a (eV) represents the energy gain per atom for this additional hydrogen with respect to the surface preoccupied by 1 ML hydrogen. Two numbers given to z_H (Å) represent the vertical heights of the surface and the subsurface hydrogen atoms from the first Pd layer, respectively.

θ (ML)	Site	E_a	Δd_{12}	Δd_{23}	z_H
1.25	T_d	−0.04	+8.8	+1.5	+0.25, −1.18
	O_h	+0.17	+5.8	+2.6	+0.21, −2.24
1.50	T_d	−0.04	+12.9	+1.8	+0.40, −1.23
	O_h	+0.16	+6.9	+5.2	+0.20, −2.36

TABLE III. Surface relaxations of the clean and H-covered Rh(100) surfaces. The calculations represent a H/Rh(100) system where 1 ML hydrogen is adsorbed on the hollow site. The exact H coverages for the LEED experiments (Refs. 13 and 14) are unknown.

	Clean Rh(100)		H/Rh(100)		
Methods	Δd_{12}	Δd_{23}	Δd_{12}	Δd_{23}	z_H
Present theory	−4.0	+0.3	+0.7	−1.0	+0.50
DFT-FLMTO[a]	−3.5		+1.1		+0.38
DFT-USPP[b]	−3.9	+0.0	+0.5	−1.0	+0.51
LEED[c]	+0.5±1.0	+0.0±1.5			
LEED[d]	−1.2±1.6	+0.0±1.6			
LEED[e]	+1.0±0.6	−0.7±0.5	+4.1±1.0	−2.2±1.0	+0.88±0.05
LEED[f]	−1.6				+0.50
PED[g]	−1.4±3.6				

[a] Reference 5.
[b] Reference 6.
[c] Reference 11.
[d] Reference 12.
[e] Reference 13.
[f] Reference 14.
[g] Reference 15.

oretical studies[4–6,25,26] predicted relatively large contractions of $\Delta d_{12}=-5\%--3\%$. Hydrogen issue was also addressed for this surface[25] as a possible origin of the discrepancy between experiment and theory, which was supported by theoretical calculations[5,6] that the Rh(100) surface shows a small expansion of $\Delta d_{12}\sim 1\%$ upon 1 ML hydrogen adsorption. Here, we extend our DFT study to the H adsorbed Rh(100) surfaces.

The hollow site is known to be preferred for hydrogen adsorption on Rh(100) in most experimental observations,[13,14,28,29] although there is a recent report that the bridge site is preferred at high coverages.[30] The saturation coverage of hydrogen is somewhat dispersive as 0.80–1.22 ML.[14,27,28,30] Let us first consider as a reference system the Rh(100) surface with 1 ML hydrogen. We find that the hollow site is more stable by 0.04 eV than the bridge site at this coverage. Table III shows the calculated surface relaxations of the H-covered and clean Rh(100) surfaces in comparison with previous theories and experiments. Theoretical calculations predict very similar surface relaxations, a large top-layer contraction of $-4.0\%--3.5\%$ for the clean Rh(100) surface and a small expansion of 0.5%–1.1% for the H-covered surface. It is noticeable in experimental data that the LEED study of Teeter *et al.*[13] reported an expansion of $\Delta d_{12}=4.1\%$ for H/Rh(100), significantly large compared to the theoretical values obtained for $\theta=1$ ML. The exact H coverage of the H-saturated LEED sample of Teeter *et al.*[13] was unknown, but the relatively large values of z_H as well as Δd_{12} and Δd_{23} strongly suggest that the H coverage is much above 1 ML.

We next consider the coverage dependence of the H-induced surface relaxation of Rh(100) up to $\theta=1$ ML. Figure 4 shows Δd_{12} at different coverages of H/Rh(100) with H on the hollow site. Like the Pd(100) case, Δd_{12} increases linearly with coverage, allowing an easy estimation of the H coverage corresponding to a measured Δd_{12}. As indicated in Fig. 4, the hydrogen coverages of the Rh(100) samples used in previous LEED[11–14] and PED[15] experiments are estimated by interpolation as $\theta\sim 0.54$, 0.58, 0.62, 0.98, and 1.08 ML from the measurements of $\Delta d_{12}\sim -1.6\%$, −1.4%, −1.2%, +0.5%, and +1.0%, respectively. The estimated H coverages of 0.54–1.08 ML are comparable to those predicted for Pd(100). In conclusion, the Pd(100) and Rh(100) surfaces reveal very similar H effects. Both surfaces are susceptible to contamination by a relatively large amount of hydrogen, and

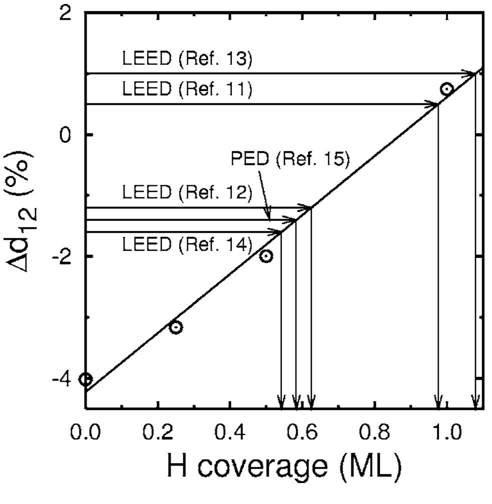

FIG. 4. Top-layer relaxation Δd_{12} of H/Rh(100) as a function of coverage. Hydrogen is assumed to adsorb on the hollow site. Circles represent the calculated points which fit to a linear curve. The amount of remaining hydrogen atoms in previous LEED and PED samples are interpolated from the linear relation.

the H contamination leads to a large expansion of the top interlayer spacing.

Finally, it is an interesting question how hydrogen affects the (100) surface of Ag, the other nearest neighbor of Pd in the Periodic Table. We notice that the Ag(100) surface is not in line with Pd(100) and Rh(100) in the surface relaxation. Previous theories[4,31,32] predicted a small contraction of the first interlayer spacing (Δd_{12}=−2.2%–−1.3%) for the clean Ag(100) surface, which is relatively close to the experimental result of 0±1.5% (Ref. 33). In order to examine the effect of hydrogen, we consider the adsorption of H on Ag(100) at θ=1 ML. The most stable is the hollow site, and Δd_{12} is calculated as 7.8%, significantly expanded from that (−1.6%) of the clean surface. That is, if contaminated by hydrogen, Ag(100) would undergo a large top-layer expansion. In our calculations, however, such hydrogen contamination is unlikely on Ag(100). The calculated adsorption energy is −0.34 eV per hydrogen atom, the negative sign of which means that the dissociative adsorption of H_2 is energetically improbable. The unlikeliness of hydrogen adsorption on Ag(100) was also demonstrated in a quantum dynamic simulation study of Eichler *et al.*[34] where dissociation barriers and sticking probabilities of H_2 to the Rh, Pd, and Ag(100) surfaces were examined over various pathways. The dissociation barriers for H_2 were calculated as 0–0.13 eV for Rh, 0–0.25 eV for Pd, and above 1.1 eV for Ag, and the sticking probabilities of H_2 with a thermal energy below 0.05 eV were ~0.7 for Rh, ~0.6 for Pd, and ~0 for Ag. Thus, we conclude that the Ag(100) surface is not affected by hydrogen below or at room temperature even if a large amount of H_2 remains in the chamber.

IV. SUMMARY

We have studied the effect of surface hydrogen on the relaxation of the (100) surfaces of Rh, Pd, and Ag, the last three consecutive 4*d* transition-metal elements. We found that the first interlayer spacings of Pd(100) and Rh(100) expand linearly with hydrogen coverage. This result was used to estimate the extent of H contamination of the surface samples investigated in previous LEED and PED experiments. Our estimation of high hydrogen coverages of 0.5–1.1 ML for these samples calls for a very careful surface treatment when preparing clean Pd(100) and Rh(100) surfaces. In the Ag(100) surface, hydrogen adsorption could result in a significantly large top-layer expansion, but such H effect is not realized in experiment since a dissociative adsorption of H_2 on Ag(100) is not probable.

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