Theoretical analysis of hydrogen chemisorption on Pd(111), Re(0001) and Pd_{ML}/Re(0001), Re_{ML}/Pd(111) pseudomorphic overlayers

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Gradient-corrected density-functional theory (DFT-GGA) periodic slab calculations have been used to analyze the binding of atomic hydrogen on monometallic Pd(111), Re(0001), and bimetallic Pd_{ML}/Re(0001) [pseudomorphic monolayer of Pd(111) on Re(0001)] and Re_{ML}/Pd(111) surfaces. The computed binding energies of atomic hydrogen adsorbed in the fcc hollow site, at 100% surface coverage, on the Pd(111), Re(0001), Pd_{ML}/Re(0001), and Re_{ML}/Pd(111) surfaces, are -2.66, -2.82, -2.25, and -2.78 eV, respectively. Formal chemisorption theory was used to correlate the predicted binding energy with the location of the d-band center of the bare metal surfaces, using a model developed by Hammer and Nørskov. The DFT-computed adsorption energies were also analyzed on the basis of the density of states (DOS) at the Fermi level for the clean metal surfaces. The results indicate a clear correlation between the d-band center of the surface metal atoms and the hydrogen chemisorption energy. The further the d-band center is from the Fermi level, the weaker is the chemisorption bond of atomic hydrogen on the surface. Although the DOS at the Fermi level may be related to the location of the d-band, it does not appear to provide an independent parameter for assessing surface reactivity. The weak chemisorption of hydrogen on the Pd_{ML}/Re(0001) surface relates to substantial lowering of the d-band center of Pd, when it is pseudomorphically deposited as a monolayer on a Re substrate. [S0163-1829(99)00431-2]

INTRODUCTION

The adsorption of hydrogen on monometallic transition-metal surfaces has been studied extensively over the past few decades, using both theoretical[1–13] and experimental methods.[14–20] From the theoretical standpoint, it provides a relatively uncomplicated system to analyze the dissociative chemisorption of simple adsorbates on metal surfaces. For heterogeneous catalysis, these studies have provided new information on the dissociative adsorption of hydrogen, an important elementary step in surface-catalyzed hydrogenation reactions. However, many processes in the petrochemical and fine-chemicals synthesis industry are carried out over supported bimetallic catalysts.[21] These include acetylene cyclization to benzene (Pd-Au), reforming for aromatics (Pt-Re), Fischer-Tropsch synthesis (Co-Ni), steam reforming of methane (Ni-Au), and maleic hydrogenation to tetrahydrofuran (Pd-Re).[21–23] UHV single-crystal experiments and theoretical calculations have identified that bimetallic surfaces can exhibit significantly different reactivity than either monometallic component.[24–29]

In recent years, surface-science techniques have attained a level of sophistication whereby well-defined bimetallic alloyed surfaces and pseudomorphic overlayers can be synthe-sized and examined under UHV conditions.[30–32] Adsorption energies on well-characterized bimetallic surfaces are now available to benchmark quantum-chemical predictions. For example, Goodman and co-workers[24,31] have studied the chemisorption of CO on a number of bimetallic systems composed of pseudomorphic overlayers of one transition metal over another. They demonstrated that the trends in chemisorption energy correspond to core-level shifts (determined using XPS) for the surface metal atoms.[24] The process of adsorption of molecules, such as CO, on metal surfaces is elegantly described by the principles of formal chemisorption theory.[33–36] Following the theory, it has been established that the dominant contributions to molecular adsorption, in a number of cases, are through electron-donation and backdonation interactions of the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) levels of the adsorbate with the valence sp and d bands of the metal. Using first-principles density-functional-theory (DFT) calculations, Hammer and Nørskov showed that the trends in CO binding energies are closely coupled to the interaction energy of the valence 5σ and $2\pi^*$ orbitals of CO with the valence sp and d band of the surface metal atoms.[37] Using concepts developed from formal chemisorption theory, they were able to demonstrate that the changes in

CO chemisorption energy for a number of monometallic and bimetallic systems correlate with shifts in the *d*-band center of the clean metal surface.[13,37,38] Recent studies have validated the effectiveness of the Hammer-Nørskov model in the analysis of atomic and molecular chemisorption on metal surfaces.[10,39]

In this paper we examine the binding of atomic hydrogen on the close-packed surfaces of Pd(111) and Re(0001) and pseudomorphic bimetallic monolayers of Pd-on-Re [Pd_{ML}/Re(0001)] and Re-on-Pd [Re_{ML}/Pd(111)]. The trends in hydrogen chemisorption energy are discussed using the Hammer-Nørskov model.[13,36,40] The surface reactivity of a metal in many situations has been cited to follow the density of states (DOS) at the Fermi level.[41] Therefore, we have also examined the relationship between the hydrogen chemisorption energy and the DOS at the Fermi level.

COMPUTATIONAL DETAILS

Gradient-corrected periodic DFT slab calculations were used to determine all the structural, electronic, and energetic results reported in this paper. The Kohn-Sham equations were solved using a plane-wave basis set of kinetic energy not exceeding 40 Ry.[42] Nonlocal corrections to the exchange-correlation energy, due to Perdew and Wang, were included self-consistently within the computations.[43] For a (1×1) unit cell of Pd(111) and Re(0001), the total energy was calculated to be convergent for 54 *k* points in the first Brillouin zone and was therefore used for all simulations. The description of atom-centered, core electronic states using a plane-wave basis expansion would require an enormous energy cutoff. Since the states actively involved in interaction with adsorbate orbitals are the valence electronic states, the nucleus and core-electronic states may be described by a norm-conserving pseudopotential, without inducing significant error in the computed adsorption energies. The pseudopotential was constructed by performing rigorous all-electron calculations on an isolated atom.[44–47] For details on the calculation scheme, see Ref. 48.

The monometallic Pd(111) and Re(0001) surfaces are described by periodic slabs containing four metal layers each. The lowermost layers of the slab were constrained to the bulk geometry while the remaining layers were allowed to relax using the Hellman-Feynman forces computed at each geometry step. The bimetallic pseudomorphic overlayers were constructed by adding a monolayer of the appropriate metal to the four-layer Pd(111) and Re(0001) slabs. The bimetallic surfaces were also relaxed to determine the optimized interlayer distances for the bimetallic system. Adsorbate-induced surface relaxations were explicitly determined for each of the surfaces and are reported in the paper.

RESULTS AND ANALYSIS

Clean slab results

Geometric and energetic parameters

The surfaces examined in this study are illustrated in Fig. 1. The monometallic Pd(111) and Re(0001) slabs are each composed of four metal layers. The bimetallic Pd_{ML}/Re(0001) and Re_{ML}/Pd(111) surfaces contain five metal layers, the overlayer being located at the idealized
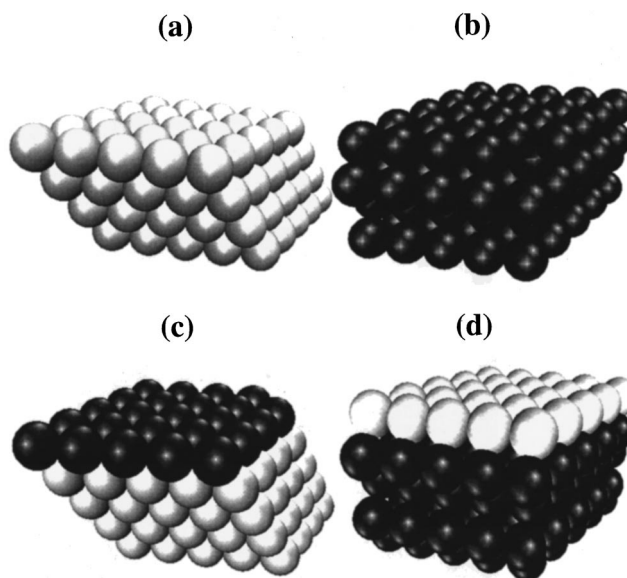

FIG. 1. Pd-Re slabs examined for hydrogen chemisorption. ● = Re; ○ = Pd. (a) Four-layer Pd(111) slab; (b) four-layer Re(0001) slab; (c) monolayer Re(0001) on Pd(111) four-layer slab; and (d) monolayer Pd(111) on Re(0001) four-layer slab.

pseudomorphic position on the substrate. In this section, the structural, energetic, and electronic parameters for the optimized bare slabs (i.e., without chemisorbed hydrogen) are summarized.

For Pd(111) and Re(0001), the interatomic distance within each layer was fixed to the bulk experimental bond distance of 2.75 and 2.76 Å, respectively. Optimization of the lattice parameter for bulk Pd resulted in a lattice constant that was about 1.5% higher than the experimental lattice parameter. It has recently been demonstrated that the adsorption energies of atomic and molecular adsorbates on metal surfaces are sensitive to strain in the metal lattice.[49] At the initial geometry, the interlayer distances were set to the experimental bulk value of 2.245 Å for Pd(111) and 2.23 Å for Re(0001). Subsequently, the geometry was optimized to determine the interlayer relaxations for each of the structures. In a periodic slab calculation, the lowermost metal layer is identical to the topmost layer by virtue of symmetry. Complete structural relaxation of the slab would, therefore, lead to identical relaxations for the top and bottom layers. To provide a better description of a multilayered metal surface, we have constrained the lowermost layers of the slab to the bulk geometry. In all calculations reported herein, every layer except the lowermost two was relaxed during the optimization procedure. For the close-packed surfaces, the interlayer relaxations are expected to be nominal beyond the second layer, so fixing the lower layers of the slab to the bulk distances is not expected to introduce significant error in surface relaxation predictions.

The optimized interlayer distances for the slabs are tabulated in Table I. Percent relaxation values are computed relative to the experimental bulk interlayer distance. DFT calculations indicate that there is very little surface relaxation for the close-packed Pd(111) surface, consistent with experimental low-energy-electron-diffraction (LEED) measurements.[50] The topmost layer of the Pd(111) surface is observed to expand by 3% (Table I). This is comparable to the

TABLE I. DFT-GGA computed structural and energetic parameters for bare slabs of Pd(111), Re(0001), Pd_{ML}/Re(0001), and Re_{ML}/Pd(111).

	Interlayer distance (% relaxation)[a] (Å)			Surface energy (eV/atom)
Surface	First to second layer	Second to third layer	Third to fourth layer	
Pd(111)	2.315 (+3.1%)	2.27 (+1.13%)	2.245 (c)[b]	0.52
Re(0001)	2.065 (−7.4%)	2.317 (+3.9%)	2.2299 (c)	1.13
Pd_{ML}/Re(0001)	2.252 (+0.9%)	2.152 (−3.5%)	2.275 (+2.02%)	
Re_{ML}/Pd(111)	2.160 (−3.8%)	2.282 (+1.6%)	2.281 (+1.6%)	

[a]% relaxation represents % change relative to idealized interlayer distance in bulk. Positive numbers correspond to surface expansion away from the bulk substrate.

[b](c) indicates that the indicated distance was constrained during the geometry optimization procedure.

1.3% expansion measured by Ohtani *et al.* using LEED (Ref. 50) and the 1% relaxation computed by Paul and Sautet using density-functional slab calculations.[1] For the Re(0001) surface, the relaxations are larger than that of Pd(111), due to the stronger interactions of the surface layer with the substrate. Unlike the surface expansion in Pd(111), the top layer in Re(0001) contracts to the bulk by 7.4%. This is in good agreement with the 7.1% contraction for Re(0001) calculated by Wu and Freeman using FLAPW-DFT.[41] Experimental LEED measurements indicate that the surface layer in Re(1010) contracts by 16%.[51] For the close-packed Re(0001) surface, we expect the relaxation to be smaller and in better agreement with our computed value. To compensate for the increased electronic charge density due to contraction of the surface layer in Re(0001), the second Re layer expands away from the third metal layer by 4%.

For the bimetallic Pd-Re slabs, the surface expansion of the Pd_{ML}/Re(0001) surface is lower than the Pd(111) surface due to stronger bonding with the substrate for the bimetallic overlayer. The contraction of the surface layer of the Re_{ML}/Pd(111) slab, however, is lower in magnitude than the Re(0001) surface, indicating stronger surface-substrate interaction in monometallic Re(0001). The metal layers of the substrate, for the pseudomorphic overlayer slabs, exhibit relaxations similar to the corresponding monometallic systems, but smaller in magnitude. For example, the second metal layer (i.e., first Re layer from the surface) of the Pd_{ML}/Re(0001) slab contracts by 3.5%, which is roughly half the relaxation of the surface layer of the Re(0001) slab (−7.4%). Similarly, the second metal layer of the Re_{ML}/Pd(111) surface expands by 1.6%, which is approximately half the expansion of the surface layer of the Pd(111) surface (+3.1%). The interlayer relaxations determined for

the Pd_{ML}/Re(0001) surface are consistent with those calculated by Wu and Freeman.[41] The Pd-Re interlayer distance, in the bimetallic slabs, is observed to be smaller for the Re_{ML}/Pd(111) surface, in comparison to the Pd_{ML}/Re(0001) surface, which suggests stronger Pd-Re interaction for the Re_{ML}/Pd(111) surface.

In Table I, we have tabulated the DFT-GGA computed surface energies of the Pd(111) and Re(0001) surfaces. The surface energies were calculated by taking the difference between the total energy of the four-layer slab and the total energy of the corresponding four layers of bulk metal, and dividing the result by 2 (to account for the two exposed surfaces in the slab). The computed surface energies for Pd(111) and Re(0001) are 0.52 and 1.13 eV/atom, respectively. These numbers are in reasonable agreement with previously reported theoretical values of 0.77 eV/atom [for Pd(111)] and 1.34 eV/atom [for Re(0001)], computed by Skriver and Rosengaard using linear-muffin-tin-orbital (LMTO) methods.[52]

Electronic properties

Table II summarizes the electronic properties for the bare Pd(111), Re(0001), Pd_{ML}/Re(0001), and Re_{ML}/Pd(111) slabs. The DFT-GGA (generalized gradient approximation) computed work function for Pd(111) (5.42 eV) is in agreement with the previously reported theoretical value of 5.53 eV (Ref. 52) and about 0.5 eV lower than the experimental value of 5.90 eV.[53] The work function for Re(0001) reported here (5.07 eV) is in good agreement with reported theoretical (5.09 eV) (Ref. 41) and experimental (4.96 eV) (Ref. 54) values. In the analysis of chemisorption of adsorbates on metal surfaces, the location of the *d* band is an important parameter that determines the extent of interaction with the adsorbate orbital states for electron donation and backdonation.[13,36,38] We have therefore computed the posi-

TABLE II. DFT-GGA computed electronic properties of bare Pd(111), Re(0001), Pd_{ML}/Re(0001), and Re_{ML}/Pd(111) surfaces.

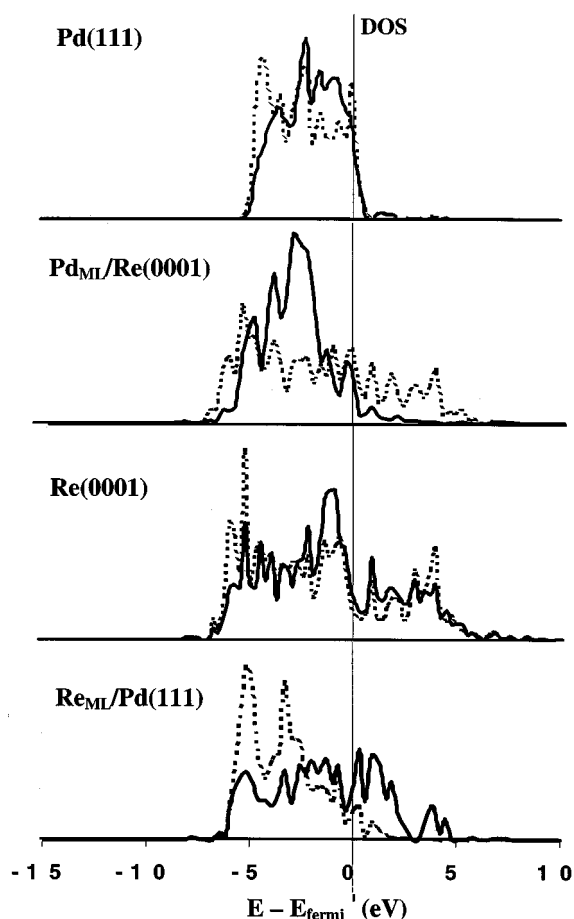| Surface	Work function (eV)	*d*-band center relative to E_f (eV)		*d*-band filling(fraction)		Density of *d* states at Fermi level (states/eV)
		First layer	Second layer	First layer	Second layer	
Pd(111)	5.42	−1.98	−2.39	0.9613	0.9674	1.7163
Re(0001)	5.07	−1.16	−1.62	0.6998	0.7208	0.5847
Pd_{ML}/Re(0001)	5.23	−2.70	−1.65	0.9608	0.7255	0.8752
Re_{ML}/Pd(111)	5.65	−1.41	−3.28	0.6789	0.9494	0.9957

FIG. 2. Electronic density of states (DOS) projected to the d band of bare slabs. Solid lines indicate DOS projected to d band of the topmost layer. Dotted lines correspond to d band of the second metal layer.

tion of the d-band center relative to the Fermi level for all the surfaces examined herein. The d-band center is located by taking the first moment of the normalized projected density of states (DOS) about the Fermi level. The fractional filling of the d band was also determined by integrating the area under the projected DOS up to the Fermi level. In Fig. 2, we have plotted the DOS projected to the d band for each of the bare slabs. The projections on the d band of the first and second metal layers are shown in the diagram. For the Pd(111) and Re(0001) surfaces, the d bands are slightly narrower for the surface layer when compared to the bulklike second layer. This is because of the incomplete coordination of the surface metal atoms, which have only nine nearest-neighbor metal atoms as compared to the bulk metal atoms, which have twelve. Since the fractional filling of the d band is practically the same for the surface and second layer of the Pd(111) slab, the narrowing of the surface d band shifts the d-band center closer to the Fermi level by 0.41 eV.[55] This is also observed for the Re(0001) surface, where the d-band center for the top layer is 0.46 eV closer to the Fermi level than the second layer.

A comparison of the d band for the surface layer of monometallic Pd(111) and the bimetallic $Pd_{ML}/Re(0001)$ reveals an interesting change in the d-band structure for the bimetallic surface. The strong electronic interaction of the Pd overlayer with the Re substrate in the bimetallic slab causes a broadening of the d band for the surface metal atoms. This was also reported earlier by Wu and Freeman on the basis of their FLAPW-DFT calculations.[41] Since the top-layer d-band filling in either case is practically unchanged, the d-band center for the bimetallic $Pd_{ML}/Re(0001)$ surface is located 0.72 eV below that of Pd(111), where the values calculated are relative to the Fermi level. This is fairly close to the d-band shift (-0.82 eV) computed by Ruban et al., using LMTO calculations, for a similar system, i.e., $Pd_{ML}/Ru(0001)$.[55] An analogous shift in the surface d-band center, although smaller in magnitude (0.25 eV), is also observed for the $Re_{ML}/Pd(111)$ surface as compared to the Re(0001) surface. The d-band filling for Re is closer to 0.5, so any broadening of the d band, because of bimetallic interaction, would have a less pronounced effect on the location of the d-band center.[55]

A comparison of the d-band center for the second layer of the Re(0001) and $Pd_{ML}/Re(0001)$ surface indicates very little influence of the surface metal atoms on the d band. The shift, however, is evident for the second metal layer of the $Re_{ML}/Pd(111)$ surface as compared to Pd(111). The d band of the second layer of the $Re_{ML}/Pd(111)$ slab is similar in profile to the surface layer of the $Pd_{ML}/Re(0001)$ surface (Fig. 2). This shows that the Pd-Re electronic interaction in the bimetallic slabs only has a marginal effect on the d band of Re, irrespective of whether Re is the overlayer or the substrate. The electronic perturbation is predominantly in the Pd layer that is directly bound to Re in the bimetallic system.

From frontier orbital theory,[33,35,56] it is known that the orbital states of a metal directly involved in electron donation and backdonation interactions with the adsorbate orbitals are the ones closest to the Fermi level. It is therefore not surprising that chemisorption and surface reactivity have in some cases been correlated to the density of electronic states at the Fermi level.[41] The d band of the surface layer of $Pd_{ML}/Re(0001)$ exhibits a reduced density of electronic states at the Fermi level as compared to the surface layer of the Pd(111) surface (Fig. 2). On the other hand, the density of states at the Fermi level for the $Re_{ML}/Pd(111)$ surface is slightly higher than the corresponding number for the Re(0001) surface.

Hydrogen chemisorption results

Geometric and energetic information

Ultrahigh-vacuum (UHV) experiments and density-functional calculations have unambiguously established that the threefold fcc hollow site is the most favorable adsorption site for hydrogen chemisorption on Pd(111).[1–4,9,57] For Re(0001), we find that the fcc hollow site is 0.25 eV more stable than the twofold bridge site. The low coordination atop site is not as favorable as the higher coordination sites for adatom binding on transition metals, and was not examined. We have, therefore, focused this study on the adsorption of hydrogen in the threefold fcc site alone, for all the metal surfaces.

To ascertain the effect of the number of metal layers on adsorbate binding energy, we studied the adsorption of atomic hydrogen on Pd(111) slabs containing between two and five metal layers. Figure 3(a) shows the binding energy for atomic hydrogen as a function of the number of metal
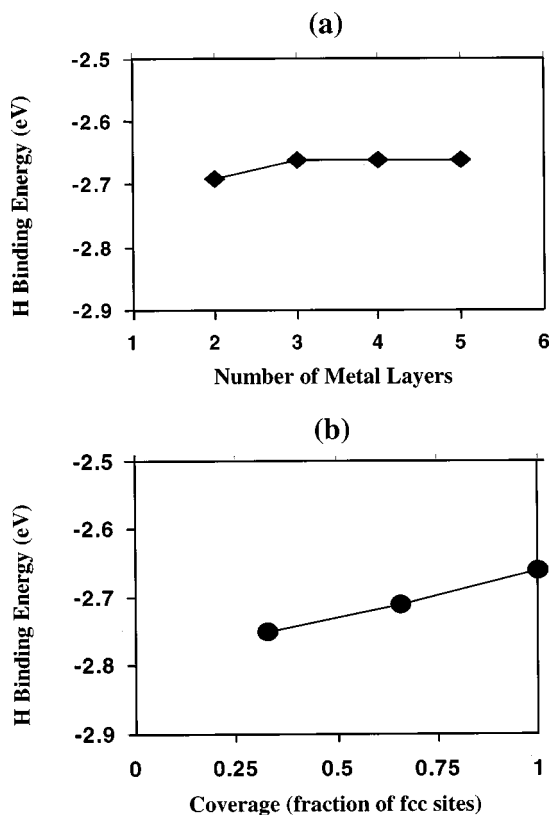
(a)

(b)

FIG. 3. (a) Hydrogen chemisorption energy on Pd(111), for 100% fcc-site coverage, as a function of the number of metal layers in a slab. (b) Hydrogen chemisorption energy as a function of surface coverage for Pd(111) three-layer slab.

layers. The adsorption energy is observed to be invariant beyond three metal layers, indicating that the slabs modeled here are adequate for the purpose of hydrogen chemisorption analysis. Our results are consistent with the observations of Paul and Sautet, who conducted a similar analysis.[1] The effect of surface coverage on hydrogen binding energy was also explicitly examined on a relaxed Pd(111) three-layer slab [Fig. 3(b)]. The binding energy of atomic hydrogen increases as we decrease surface coverage, thus indicating repulsive interactions at higher coverages [Fig. 3(b)]. In decreasing the surface coverage from 100% (1×1 unit cell) to 33% ($\sqrt{3} \times \sqrt{3}$ unit cell), the binding energy of hydrogen was observed to increase by 0.11 eV. To resolve the contribution of through-space H-H repulsion on the adsorption energy, we examined gas phase hydrogen atoms (i.e., without

the Pd surface) arranged in a (1×1) structure. The total energy for hydrogen in this structure was found to be 0.2 eV less favorable than the energy for an isolated hydrogen atom, consistent with the observations of Paul and Sautet.[1] Thus the most dominant contribution to the change in adsorption energy due to surface coverage is due to through-space H-H repulsion at 100% coverage.[1] Since this contribution is independent of the nature of the metal surface, the effect of surface coverage on adsorption energy was not independently examined for each surface.

The changes in the surface structure due to chemisorption of hydrogen were determined by completely optimizing the adsorbate and the metal surface. The two lowermost metal layers of the slabs were constrained to the bulk interlayer distances, while the remaining layers, including the adsorbate layer, were relaxed. In Table III, we have summarized the key geometric and energetic parameters for hydrogen binding on the monometallic and bimetallic surfaces. To quantify the degree of adsorbate-induced surface relaxation, we have provided % relaxation numbers in Table III. It is important to note that these percentages are computed relative to the corresponding interlayer distance for the bare slab, and not the bulk interlayer distance. Table III shows that the adsorbate-induced surface relaxation is very small for hydrogen on Pd(111). For all the slabs, the relaxation is positive (i.e., expansion), consistent with the fact that the strong bonding of the surface metal layer with the adsorbate weakens its interactions with the substrate layers. The second metal layer for all surfaces except $Re_{ML}/Pd(111)$ exhibits a compensatory inward relaxation. Table III also shows the optimized M-H bond distances for each of the slabs. The M-H bond distances are about 0.1 Å longer for the Re surfaces than Pd. The H-Re bond distance computed here is in agreement with the measurements of Doll *et al.*[18] The M-H bond distances for the bimetallic slabs are slightly longer than those on monometallic slabs. This is consistent with the weaker adsorption energies on the bimetallic surfaces in comparison to the corresponding monometallic slabs.

The binding of atomic hydrogen is strongest on the Re(0001) surface with a binding energy of -2.82 eV. The binding energy on the $Re_{ML}/Pd(111)$ surface is slightly weaker, with a value of -2.78 eV. Considering the accuracy of the DFT methodology, and the small difference in binding energy, it is reasonable to assume that both Re(0001) and $Re_{ML}/Pd(111)$ demonstrate similar strengths of adsorption for hydrogen. The adsorption energy computed for hydrogen on Re(0001) matches well with the experimental value of

TABLE III. Geometric and energetic information for hydrogen chemisorption on Pd(111), Re(0001), $Pd_{ML}/Re(0001)$, and $Re_{ML}/Pd(111)$ slabs.

	Interlayer distance (Å) (% relaxation)[a]				M-H bond distance (Å)	Hydrogen chemisorption energy (eV)
Surface	H to first M layer	First to second M layer	Second to third M layer	Third to fourth M layer		
Pd(111)	0.858	2.327 (+0.5)	2.242 (−1.23)	2.245 (c)[b]	1.80	−2.66
Re(0001)	1.059	2.125 (+2.9)	2.295 (−0.95)	2.2299 (c)	1.91	−2.82
$Pd_{ML}/Re(0001)$	0.939	2.304 (+2.3)	2.122 (−1.39)	2.267 (−0.35)	1.85	−2.25
$Re_{ML}/Pd(111)$	1.123	2.180 (+0.93)	2.347 (+2.85)	2.316 (+1.53)	1.94	−2.78

[a]% relaxation corresponds to adsorbate-induced relaxation and is computed relative to interlayer distance for the clean slab.

[b](c) indicates that the indicated distance was constrained during the optimization procedure.
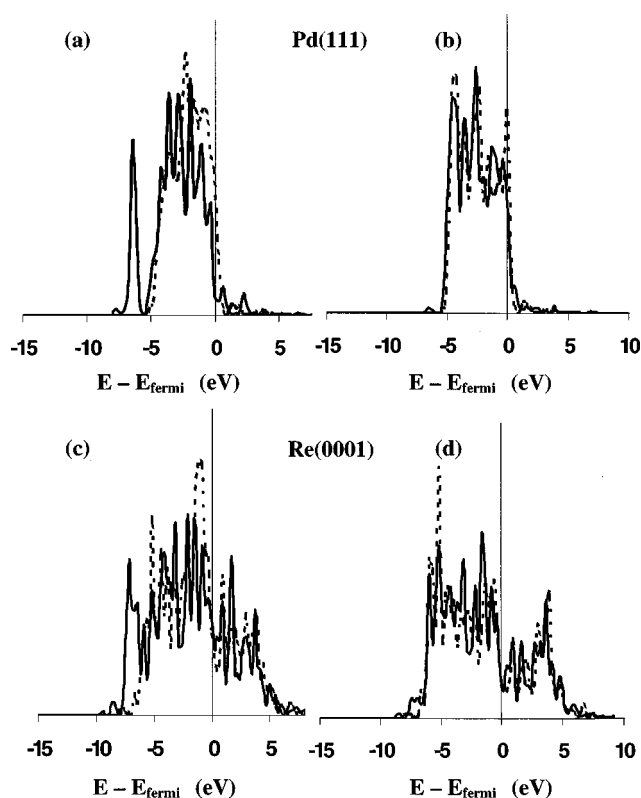
FIG. 4. Density of states (DOS) projected to the d band of the metal for bare and hydrogen-chemisorbed surfaces. Solid lines indicate projected DOS for the hydrogen-chemisorbed system. Dotted lines correspond to the bare slab. (a) d band of topmost Pd(111) layer of Pd(111) four-layer slab; (b) d band of the second Pd layer of Pd(111) four-layer slab; (c) d band of topmost Re(0001) layer of Re(0001) four-layer slab; and (d) d band of the second Re layer of Re(0001) four-layer slab.

FIG. 5. Projected DOS for hydrogen chemisorbed on Pd(111) and $Pd_{ML}/Re(0001)$ systems. Solid lines correspond to DOS projected to surface metal d band. Dotted lines correspond to DOS projected to the H $1s$ state.

-2.85 eV, estimated from the TPD data of Godbey and Somorjai.[19] The chemisorption energy for hydrogen on Pd(111) (-2.66 eV) is about 0.15 eV lower than that on Re(0001). The DFT-GGA computed value of -2.66 eV for the adsorption energy is in agreement with previously reported theoretical and experimental results.[1–4,9,57] Interestingly, the binding energy of H on $Pd_{ML}/Re(0001)$ (-2.25 eV) is weaker than that on Pd(111) by as much as 0.41 eV. Since the gas-phase dissociation energy for H_2 is 4.52 eV,[58] the results indicate that the dissociative adsorption of hydrogen on the $Pd_{ML}/Re(0001)$ is endothermic by 2 kJ/mol. For surfaces such as Au(111), where the dissociative adsorption of H_2 is endothermic, Hammer and Nørskov have shown that the process also has a high activation barrier.[13] The dissociative adsorption of H_2 is therefore likely to be difficult on the bimetallic $Pd_{ML}/Re(0001)$ surface. This is ratified by UHV single-crystal experiments that report extreme difficulty in the adsorption of hydrogen on the bimetallic $Pd_{ML}/Re(0001)$ surface.[30] The surface has also been demonstrated experimentally to exhibit weak adsorption energies for molecular adsorbates such as CO.[30,59]

Electronic properties

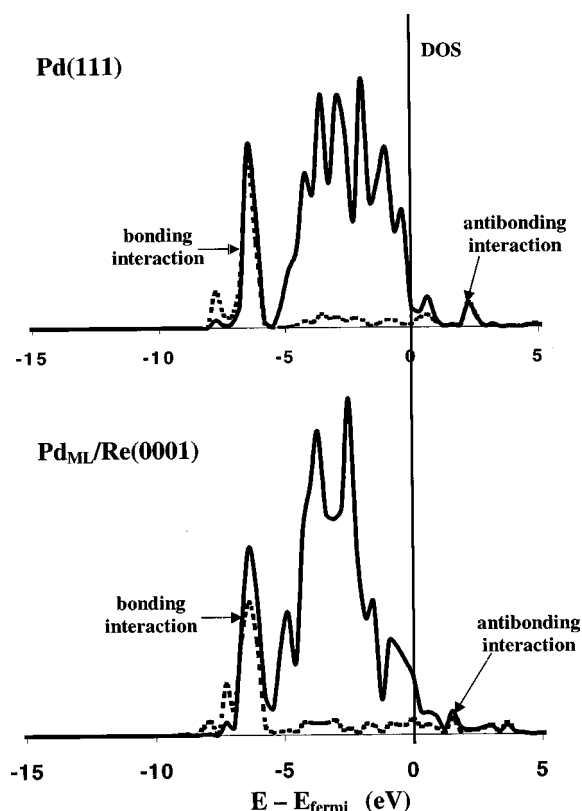Figure 4 shows the DOS projected to the d band of the surface and second metal layer of Pd(111) and Re(0001), for both the bare and hydrogen-chemisorbed systems. The solid lines correspond to the DOS for the slabs with chemisorbed hydrogen. The dotted lines indicate the corresponding DOS for the bare slabs. From Figs. 4(b) and 4(d), it is observed that there is very little perturbation in the electronic DOS for the second metal layer of Pd(111) and Re(0001) due to hydrogen chemisorption. The d bands for the surface layer of Pd(111) and Re(0001) [Figs. 4(a) and 4(c)], however, are significantly altered by hydrogen adsorption. For both surfaces, the adsorption of hydrogen results in a characteristic split-off state in the d band of the surface layer. The split-off state is located at -6.62 eV, below the Fermi level, for Pd(111) and at -8.79 eV, below the Fermi level, for Re(0001). The split-off state corresponds to the bonding overlap of the metal d band with the H $1s$ orbital. The relative position of this state is shifted further down in energy away from the Fermi level for Re(0001) as compared to Pd(111). This signifies stronger interaction of the H $1s$ state with the Re d band and is responsible for the stronger chemisorption energy. The antibonding overlap of the d band with the H $1s$ orbital results in unoccupied eigenstates located above the Fermi level. For Pd(111) and Re(0001), the antibonding states are located at 2.5 and 5 eV above the Fermi energy, respectively. The DOS computed for Pd(111) match well with previously reported experimental and theoretical DOS profiles.[1,60,61]

We now compare the DOS for hydrogen chemisorption on the monometallic versus the bimetallic surfaces. Figure 5 shows the DOS for hydrogen chemisorbed on Pd(111) and
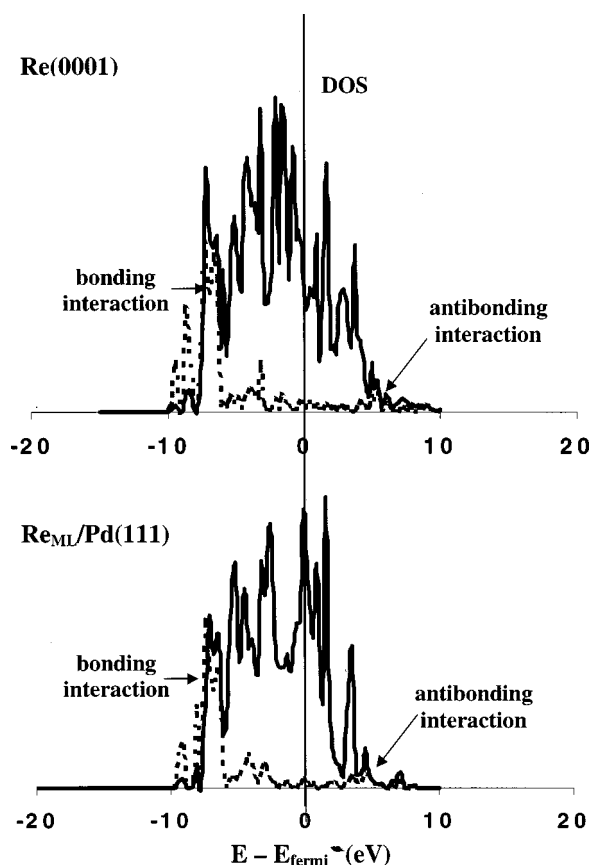
Re(0001)

FIG. 6. Projected DOS for hydrogen chemisorbed on Re(0001) and Re$_{ML}$/Pd(111) systems. Solid lines correspond to DOS projected to surface metal d band. Dotted lines correspond to DOS projected to the H $1s$ state.

Pd$_{ML}$/Re(0001). The solid lines correspond to the DOS projected to the d band of the surface layer. The dotted lines are the DOS projected to the H $1s$ state. The hybridization of the H $1s$ state with the d band of the metal results in a split-off bonding state centered at -6.62 eV for Pd(111) and -6.56 eV for Pd$_{ML}$/Re(0001). The antibonding overlap of the H $1s$ with the d band is situated above the Fermi level at 2.5 eV for Pd(111) and at about 1.5 eV for Pd$_{ML}$/Re(0001). There are clear differences in the DOS projected to the d band of the Pd(111) and Pd$_{ML}$/Re(0001) surface. The d band of the Pd$_{ML}$/Re(0001) surface is shifted away from the Fermi level in comparison to Pd(111). On the other hand, the DOS for hydrogen on Re(0001) and the Re$_{ML}$/Pd(111) surface (Fig. 6) exhibit very little difference in the d-band structure for the surface Re layer. The split-off bonding state is centered at -8.79 and -8.67 eV below the Fermi energy for Re(0001) and Re$_{ML}$/Pd(111), respectively. The antibonding state is located above the Fermi level at 5 eV for Re(0001) and at 4.5 eV for Re$_{ML}$/Pd(111).

Analysis

In the preceding section, we presented the chemisorption energy for hydrogen in the fcc hollow site on the monometallic Pd(111), Re(0001), and the bimetallic Pd$_{ML}$/Re(0001) and Re$_{ML}$/Pd(111) surfaces. DFT calculations showed that the binding of atomic hydrogen on the Re$_{ML}$/Pd(111) sur-
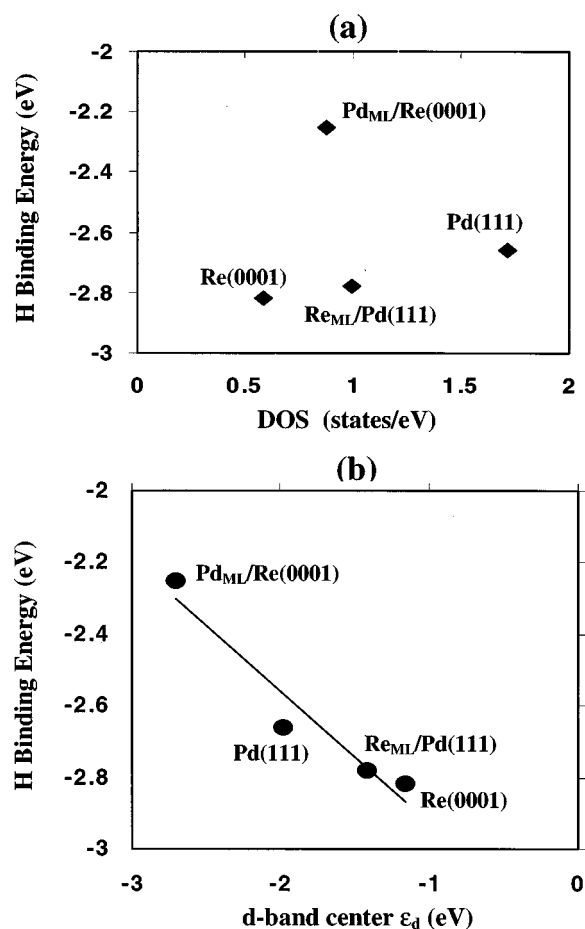
FIG. 7. (a) Binding energy of atomic hydrogen at the threefold fcc site as a function of the DOS at the Fermi level for the bare surfaces. (b) Binding energy of atomic hydrogen as a function of the d-band center for the clean metal surfaces (Hammer-Nørskov model). d-band centers are relative to the Fermi energy.

face is similar to that on Re(0001). The Pd$_{ML}$/Re(0001) surface, however, exhibited markedly reduced reactivity for hydrogen chemisorption, in comparison to Pd(111). In this section, we will examine whether the trends in atomic chemisorption energy can be correlated to the electronic properties of the clean metal surfaces. The electronic parameters of the surface that are assessed as a measure of the surface reactivity for adsorption are the surface metal d-band center (in accordance with the model of Ref. 13) and the DOS at the Fermi level.

Correlating trends in chemisorption energy to the DOS at the Fermi level

In Fig. 7(a) we have plotted the hydrogen chemisorption energy as a function of the density of d states at the Fermi level, for all the surfaces. In comparing the Pd(111) and the Pd$_{ML}$/Re(0001) surface, it is observed that the Pd$_{ML}$/Re(0001) surface has a significantly reduced projected DOS at the Fermi level. This is consistent with the fact that the interaction of hydrogen with the Pd$_{ML}$/Re(0001) surface is weaker than that with Pd(111). However, the above argument does not seem to hold when we compare the Re(0001) and Re$_{ML}$/Pd(111) surfaces, where the DOS at the Fermi

level are quite different, but the hydrogen adsorption energies are practically identical (refer Table II). Also, if we compare the DOS at the Fermi level for Pd(111) and the Re(0001) surface, we would expect stronger adsorption on the Pd(111) surface, but the contrary is found to be true. The results seem to suggest that although the DOS at the Fermi level may in some cases correlate with surface reactivity, it cannot be used as an independent measure of the reactivity of different metal surfaces.

Correlating trends in the chemisorption energy to the location of the surface metal d-band center

Using the analysis of Hammer et al.,[38] it can be shown that for small changes in the d-band center, changes in the hydrogen chemisorption energy (δE_{chem}) can be linearly correlated to shifts in the d-band center position for the metal ($\delta \varepsilon_d$),

$$\delta E_{chem} = \frac{V^2}{(\Delta \varepsilon)^2} \delta \varepsilon_d, \qquad (1)$$

where V^2 is the d-band coupling matrix element for the surface metal atom, and $\Delta \varepsilon = |\varepsilon_d - \varepsilon_a|$, ε_d, and ε_a are the location of the d-band center and the H $1s$ orbital state, respectively, measured relative to the Fermi energy.

A single linear correlation, for all the surfaces examined here, may be expected only if the value of $V^2/(\Delta \varepsilon)^2$ is approximately the same for both Pd and Re. In comparing Pd(111) and Re(0001), it is observed that[36]

$$\frac{V_{Re}^2}{V_{Pd}^2} \sim \frac{6.04}{2.78} \left(\frac{1.80}{1.91} \right)^6 = 1.522, \qquad (2)$$

where 6.04 and 2.78 are the d-band coupling matrix elements for Re and Pd, respectively, with reference to Cu,[36] and (1.80/1.91) is the ratio of the M-H bond distance for Pd(111) and Re(0001).

Since the H $1s$ state is centered at about -5 eV below the Fermi energy, after interaction with the sp electrons, the ratio

$$\left(\frac{\Delta \varepsilon_{Pd}}{\Delta \varepsilon_{Re}} \right)^2 \sim \left(\frac{5 - 1.98}{5 - 1.16} \right)^2 = 0.62. \qquad (3)$$

From Eqs. (2) and (3), it follows that the ratio

$$\left\{ \frac{\left[\frac{V_{Re}^2}{(\Delta \varepsilon_{Re})^2} \right]}{\left[\frac{V_{Pd}^2}{(\Delta \varepsilon_{Pd})^2} \right]} \right\} \sim 1.522 \times 0.62 = 0.95 \qquad (4)$$

is approximately equal to 1.0. This allows us to graph all the Pd and Re surfaces on the same plot, for analysis using the model of Ref. 13.

In Fig. 7(b), we have plotted the hydrogen binding energy as a function of the d-band center of the bare surfaces examined here. Figure 7(b) clearly shows that as the d-band center is farther from the Fermi energy, the chemisorption of atomic hydrogen is weaker on the surface. The d-band for the bare Pd$_{ML}$/Re(0001) surface is in some respect similar to

the Au(111) and the Cu(111) surface because it has a d-band center located farther away from the Fermi level than Pd(111). It is thus not surprising that the adsorption energy of atomic hydrogen on the surface is also very weak, similar to the Au(111) and Cu(111) surfaces.

CONCLUSIONS

DFT-GGA periodic slab calculations were used to analyze the binding of atomic hydrogen on monometallic Pd(111), Re(0001), and bimetallic Pd$_{ML}$/Re(0001) and Re$_{ML}$/Pd(111) surfaces at the fcc hollow site for 100% surface coverage. The binding of hydrogen is strongest on the Re surfaces, with a chemisorption energy of -2.82 eV for Re(0001) and -2.78 eV for Re$_{ML}$/Pd(111). The binding energy on Pd(111) (-2.66 eV) is about 0.15 eV weaker than that on Re(0001). The computed adsorption energies on Pd(111) and Re(0001) are in good agreement with previously published theoretical and experimental values.[1–4,9,57] Calculations indicate that the binding energy of atomic hydrogen on the Pd$_{ML}$/Re(0001) surface (-2.25 eV) is significantly weaker than that on monometallic Pd(111) and Re(0001). In fact, the binding energy of hydrogen on the surface is so low that the dissociative adsorption of H$_2$ would be 2 kJ/mol endothermic on the surface. This weak interaction of the Pd$_{ML}$/Re(0001) surface for adsorption is consistent with previously reported experimental observations for hydrogen and other molecular adsorbates, such as CO, on the bimetallic Pd$_{ML}$/Re(0001) surface.[30,59] The uncharacteristic adsorption behavior on the Pd$_{ML}$/Re(0001) surface can be explained by changes in the electronic structure near the Fermi level of the surface metal atom, which decreases the extent of bonding between the surface and the adsorbate. The change in the surface electronic structure is manifested as a shifting of the d-band center away from the Fermi level. The d band of the surface Pd atom of the bare Pd$_{ML}$/Re(0001) surface is similar to Au(111) or Cu(111), with a d band center located 0.72 eV farther away from the Fermi energy as compared to monometallic Pd(111). This shift of the d-band away from the Fermi level also causes attenuation in the DOS close to the Fermi level, consistent with the observation of Wu and Freeman.[41] The d band of the Re$_{ML}$/Pd(111) surface, on the other hand, is only slightly different from that of the Re(0001) surface and shows similar adsorption strengths for the binding of atomic hydrogen. An attempt to associate the hydrogen binding energy on the surfaces to the DOS at the Fermi level reveals very little correlation between these parameters. The most important conclusion of this study is that the more predominant control on atomic and molecular adsorption energies on surfaces is through modifications in the location of the d-band center for the surface.

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