

Electronic structure of Pd thin films on Re(0001) studied by high-resolution core-level and valence-band photoemission

Bongjin Simon Mun,^{1,2} Choongman Lee,³ Vojislav Stamenkovic,¹ Nenad M. Markovic,¹ and Philip N. Ross, Jr.¹

¹Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

²Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

³Semiconductor R&D Center, Samsung Electronics Co., LTD, Korea

(Received 10 March 2004; published 18 March 2005)

The electronic structures of Pd thin films grown epitaxially on a Re(0001) single-crystal surface are investigated with high-resolution photoelectron spectroscopy. A clear splitting of the Pd $3d_{5/2}$ core level is observed as the coverage of Pd increases from submonolayer to multilayer. The peak at higher binding energy is assigned to emission from the Pd layer at the interface with the Re substrate, while the other is from “bulk” Pd. The observed valence-band spectrum of the pseudomorphic Pd monolayer on Re clearly revealed a reduction in the density of states near the Fermi level and shifting of the d -band center to higher binding energy. It is possible to reconcile the seemingly contradictory core level and valence-band shifts based on the charge-density maps from the earlier full-potential linearized augmented-plane-wave band-structure calculation by Wu and Freeman. Filling of the Pd d band by electron donation from the substrate does not occur. Rather, the correct physical picture for the electronic modification is substrate-induced charge polarization in the Pd layer

DOI: 10.1103/PhysRevB.71.115420

PACS number(s): 73.20.At

INTRODUCTION

It is now well known that ultrathin metal films deposited on foreign metal substrates often display unique structural and electronic properties, consequently resulting in significantly modified chemical properties of the surface.^{1–6} In particular, when a pseudomorphic monolayer of Pd film is prepared on various transition-metal substrates, the electronic and chemical properties of the surface exhibit significantly different characteristics from the surface of bulk phase Pd.^{1,2} For example, the temperature for desorption of CO from a Pd monolayer on Re(0001) is dramatically reduced (by ~ 200 K) from that for desorption from bulk Pd, i.e., the CO chemisorption bond to the Pd surface atoms is considerably *weakened* by the Pd—Re interaction. Previously, Rodriguez and Goodman found a close correlation between the reduction in CO desorption temperature and the core-level shifts [determined by x-ray photoemission spectroscopy (XPS)] of the surface metal atoms.³ Initially, charge transfer between the Pd overlayer and the Re substrate was proposed to interpret the adlayer core-level shift (ACLS) and the attendant modified chemical bonding. Later, other theoretical models were proposed to explain the physical and chemical properties of the Pd/Re(0001) and related bimetallic systems.⁴ More recently, using first-principles density-functional-theory (DFT) calculations, Hammer and Nørskov⁵ showed that the changes in CO chemisorption energy for a number of both monometallic and bimetallic systems correlate with shifts in the surface d -band center, i.e., the first moment of the surface metal d -band density of states (DOS). Subsequently, Pallassana *et al.*⁶ presented a detailed gradient-corrected DFT periodic slab calculation of the electronic structure specifically for the Pd/Re(0001) bimetallic system, and correlated the electronic structure to the chemisorption bond of atomic hydrogen on this surface. It was shown that the d band of the surface Pd atoms on the Re substrate is

similar to that of Au(111) and Ag(111), with a d band center shifted 0.72 eV below that for the bulk Pd, with a corresponding reduction in chemisorption bond energy of 0.4 eV.

In this paper, we reexamine the electronic structure of Pd thin films on Re(0001) substrates with synchrotron-based high-resolution core-level (XPS) and valence-band ultraviolet photoemission spectroscopy photoemission. With the higher-resolution XPS measurement, the Pd $3d$ core-level spectra reveal a unique interfacial binding energy, not observed in the previous XPS measurements, as the thickness of Pd layers is increased. In addition, in the surface valence band, the Pd monolayer at the interface exhibits a modified electronic structure which is significantly different from that of the multilayer, i.e., bulk Pd (111), with a clear reduction of DOS near Fermi level and shift of the d -band center away from the Fermi level. It is shown that the experimental DOS is in complete accord with the gradient-corrected DFT periodic slab calculation of Pallassana *et al.*⁶

EXPERIMENT

The photoemission measurements were carried out in the Advance Materials Chamber (AMC), located on beamline (BL) 9.3.2. of the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory. BL 9.3.2 is a bending magnet beamline with a water-cooled spherical grating monochromator. Specifications of photon flux and energy resolution for this beamline are reported in Ref. 7. The AMC chamber was equipped with a SES100 (Scienta) hemispherical electron energy analyzer, conventional rear-view low-energy electron diffraction (LEED) optics, and a small low-rate electron beam evaporator (Oxford Applied Research Model EGC04). A clean surface of Re(0001) single crystal was prepared with repeated cycles of argon-ion sputtering, light annealing at an O_2 pressure of $\sim 1 \times 10^{-6}$ torr, followed by a short annealing at 1500 K. Surface cleanness was moni-

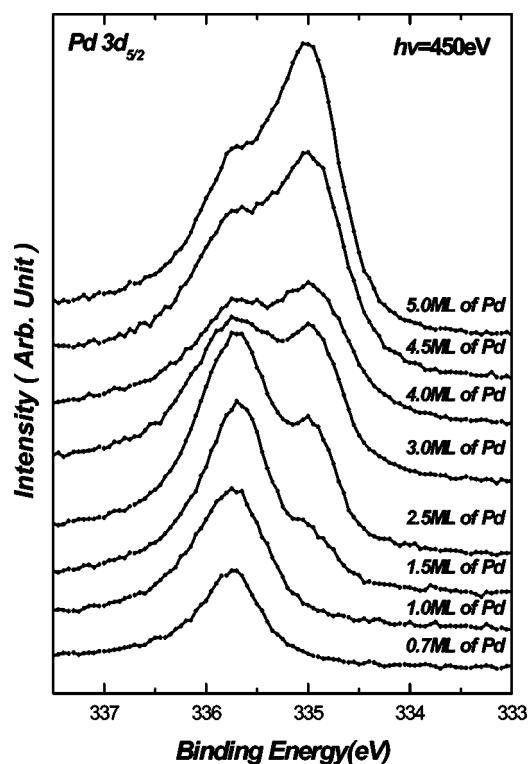


FIG. 1. The Pd $3d$ core-level spectra are shown as a function of Pd coverage on the Re(0001) surface. The photon energy ($h\nu$) is 450 eV and the electron detection angle is normal to the surface.

tored with C $1s$ and O $1s$ XPS. The clean annealed surface structure was checked with LEED, resulting in the expected sharp (1×1) hexagonal pattern. Pd was deposited on the clean surface by e -beam evaporation. During the deposition of film, the chamber pressure was $\sim 5 \times 10^{-10}$ torr and the sample temperature was ~ 300 K. The deposition rate of Pd was set to one monolayer (ML) per 7 min, which was calibrated using a quartz crystal microbalance monitor and checked *in situ* using the relative intensities of Pd and Re core-level spectra. To avoid formation of a surface alloy, no post-annealing after deposition was applied, and did not appear to be necessary to achieve epitaxial growth. The LEED pattern retained the same sharp (1×1) pattern as for the clean surface up to the highest coverages used here, nominally 4 ML of Pd. For the high-resolution photoemission spectra (PES), the total energy resolution, including the photon energy resolution, was less than ~ 0.1 eV. All PES data were taken at a chamber pressure of 2×10^{-10} torr or less.

RESULTS AND DISCUSSION

Before starting the presentation of core-level spectra, it is important to specify how we determine the adlayer core-level shift (ACLS), which is different from the surface core-level shift (SCLS). By definition, the ACLS is the difference in the core-level ionization energy between two surface atoms of two different elements, while the SCLS is the difference in ionization energies between the surface and bulk atoms of the same element.⁸ In the system studied here, the

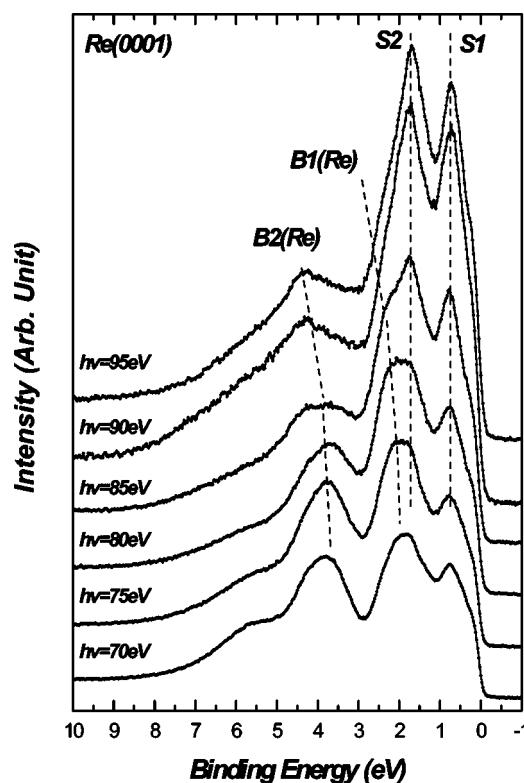


FIG. 2. The valence spectrum of a clean Re(0001) surface is measured while varying the photon energies ($h\nu$) at fixed normal emission. Two peaks at S1 (BE=0.8 eV) and S2 (BE=1.8 eV) are surface states while the peaks B1(Re) and B2(Re) are bulk bands from Re $5d$ and $6s$ hybridization, which show a dispersion in k space.

ACLS of Pd/Re(0001) is defined as the difference in ionization energy of a Pd atom on the surface of Re(0001) and on the surface of bulk Pd(111). With this definition, the screening of the core hole will be similar in both Pd/Re(0001) and Pd(111) since the emitting atom has the same reduced (surface) dimension. The ACLS then can be taken as a direct measure of the change in electronic state of the Pd atoms at the interface due to the interaction with the Re substrate.

The Pd $3d$ core-level spectra are shown in Fig. 1 as a function of Pd coverage on the Re(0001) surface. The photon energy ($h\nu$) was 450 eV (kinetic energy for Pd $3d_{5/2}$ is thus ~ 110 eV) and the electron detection angle was normal to the surface. From Fig. 1, it is clear that there are two different states of Pd on the surface of Re(0001), with population varying with coverage. Only the higher binding energy state is occupied at coverages up to 1 ML, i.e., a single Pd $3d_{5/2}$ peak position remains at BE=335.7 eV, which can reasonably be assigned to the BE of Pd atoms at the Pd/Re(0001) interface. As the coverage of Pd films increases from 1.5 ML to 2.5 ML, a new state evolves at lower binding energy, BE=335.0 eV, which by inference is reasonably assigned to emission from Pd atoms in the multilayer, i.e., from (111) oriented 3D islands of Pd.⁹ When the Pd coverage reaches 5 ML, the emission from 3D islands of Pd dominates the intensity of Pd $3d_{5/2}$ spectra. The $3d_{5/2}$ emission from Pd(111) is known to have an SCLS of about 0.3 eV,⁸ and fitting (not

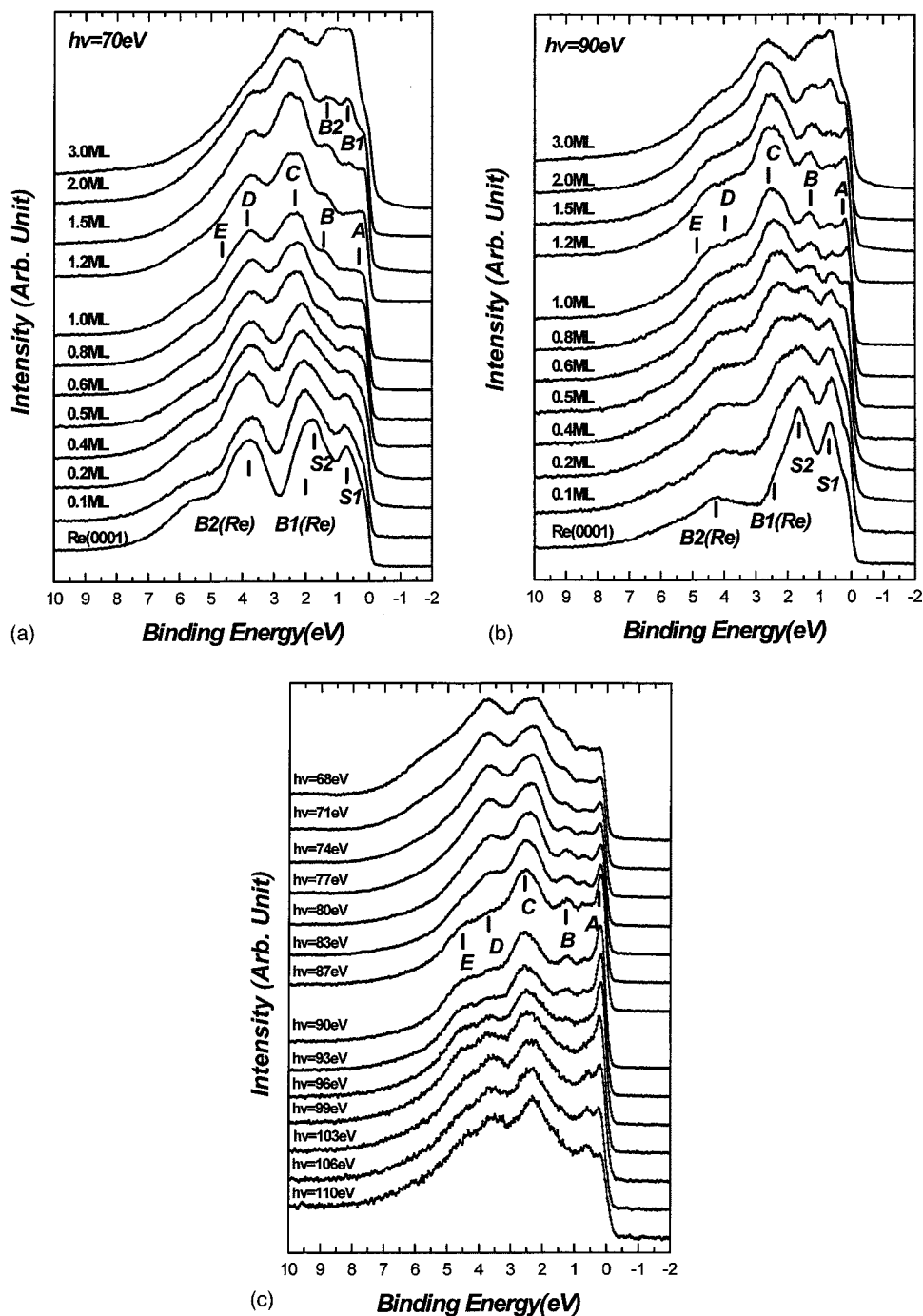


FIG. 3. The valence-band photoemission (normal to surface) spectra of Pd on Re are shown [(a) and (b)] as a function of Pd coverage at 70 eV and 90 eV photon energy and (c) at varying photon energies for 1 ML Pd coverage. Electronic states unique to the monolayer film are clearly shown.

shown) of the spectrum at 5 ML indicated a third “surface peak” is present at $BE=334.7$ eV, in close agreement with the value in Ref. 9. Thus, the ACLS for the Pd monolayer on Re(0001) is close to +1.0 eV. This is slightly higher than the value for the ACLS of a Pd thin film on Re used by Rodriguez and Goodman³ in their correlation of CO chemisorption energy with the adlayer core-level shift (0.7 eV), probably due to the higher resolution in the measurements here. During the acquisition of Pd $3d$ spectra, Re $4f$ spectra were also acquired simultaneously. However, the position of the Re $4f_{7/2}$ peak remained constant (within 0.1 eV), and this is consistent with the previous observation by Rodriguez and Goodman.³

The manner in which the relative intensities of the two Pd $3d_{5/2}$ peaks change with Pd coverage in the Fig. 1 can also be used to infer the growth mode of the Pd multilayer film on Re(0001). If the Pd film grew pseudomorphically and layer-by-layer up to a few layers, photoemission from the interfacial layer would be more dramatically attenuated than in Fig. 1(a) due to the short inelastic mean free path (IMFP) of Pd $3d$ photoelectrons at the kinetic energy of 110 eV [~ 0.35 nm (Ref. 10)]. Yet, even at 5 ML or three times the IMFP, the signal is attenuated by only a factor of 2 or so, versus the expected order of magnitude. This result implies an island growth mode (Stranski-Krastanov model¹¹), i.e., 3D islands of Pd on top of the first pseudomorphic mono-

layer growth. Of course, this is only indirect evidence of the growth mode, and a more definitive picture can be obtained with the use of scanning probe techniques. But the evidence here suggests considerable caution must be exercised in the study of the chemical properties of these metallic overlayer systems, as the electronic interactions may be highly localized to the interfacial layer, but unless film thickness is very well controlled, there may be many other surface atoms present in another (unmodified) electronic state.

In Fig. 2, the valence-band (VB) spectra of clean Re(0001) is shown with varying photon energies ($h\nu$). This photon energy dependence helps not only to identify the “surface-state” (nondispersive) contribution from the VB DOS, but also to determine the optimum photon energy for avoiding the second-order contribution from the monochromator grating. As shown in Fig. 2, the two peaks denoted S1 (BE=0.8 eV) and S2 (BE=1.8 eV) are surface states, which did not show any k -space dispersion (in this case with variation of photon energy), while the peaks denoted B1(Re) and B2(Re), which show dispersion with varying photon energy, are from the bulk bands from Re 5*d* and 6*s* hybridization.¹²

The VB photoemission spectra from Pd thin films on Re(0001) are shown in Fig. 3 as a function of Pd coverage (a) and (b) and photon energy (c). First, as manifested in Fig. 3(a) and 3(b), with given photon energy at 70 eV and 90 eV, the surface peaks characteristic of the Re VB (S1, S2) are strongly attenuated by the initial deposition of Pd films. When the Pd coverage reaches 0.5 ML, it becomes difficult to distinguish any of the Re substrate VB features in the total emission from Pd/Re(0001). As the Pd coverage nears 1.0 ML, a significant reduction in the DOS near the Fermi level and new features at A (BE=0.2 eV), B (BE=1.2 eV), and C (BE=2.5 eV) are clear. There is also enhancement of broader features (D and E) at higher binding energy that appears to be maximized at 1 ML coverage. As Pd coverage increased further to 2–3 ML, the features denoted B1 and B2 start to emerge and the total DOS starts to resemble that for Pd(111).¹³ In Fig. 3(c), which shows the VB spectra of 1.0 ML Pd at varying the incoming photon energies, all peaks identified in Fig. 3(a) and 3(b) (A–E) show little dispersion across the k space, and thus can be assigned as unique surface states of the 2D Pd layer on Re(0001) substrate. These unique states (A–E) appear to be maximized for photon energies between 70 and 90 eV and, for clarity and simplicity, we will present subsequent results using only the spectra for 70 eV and 90 eV photon energy.

To identify more clearly the partial DOS of the 2D Pd layer at the interface with Re(0001), a scaled VB spectrum of the clean Re(0001) substrate was subtracted from each spectrum and replotted as *difference* spectra in Fig. 4. It is clear that the five distinct features (A–E) can be clearly seen in the 1.0–1.5 ML *difference* spectra, indicated with bars. The states closest to the Fermi level, A–C, appear immediately upon Pd deposition and are characteristic of isolated Pd atoms, dimers, or trimers on Re(0001). The features at D (BE=3.8 eV) and E (BE=4.5 eV) start to show near 0.8 ML coverage and are most resolved at 1.0–1.2 ML coverage. Experimentally, it appears that states C–E are the most characteristic of the 2D Pd layer at the interface. The spectra at

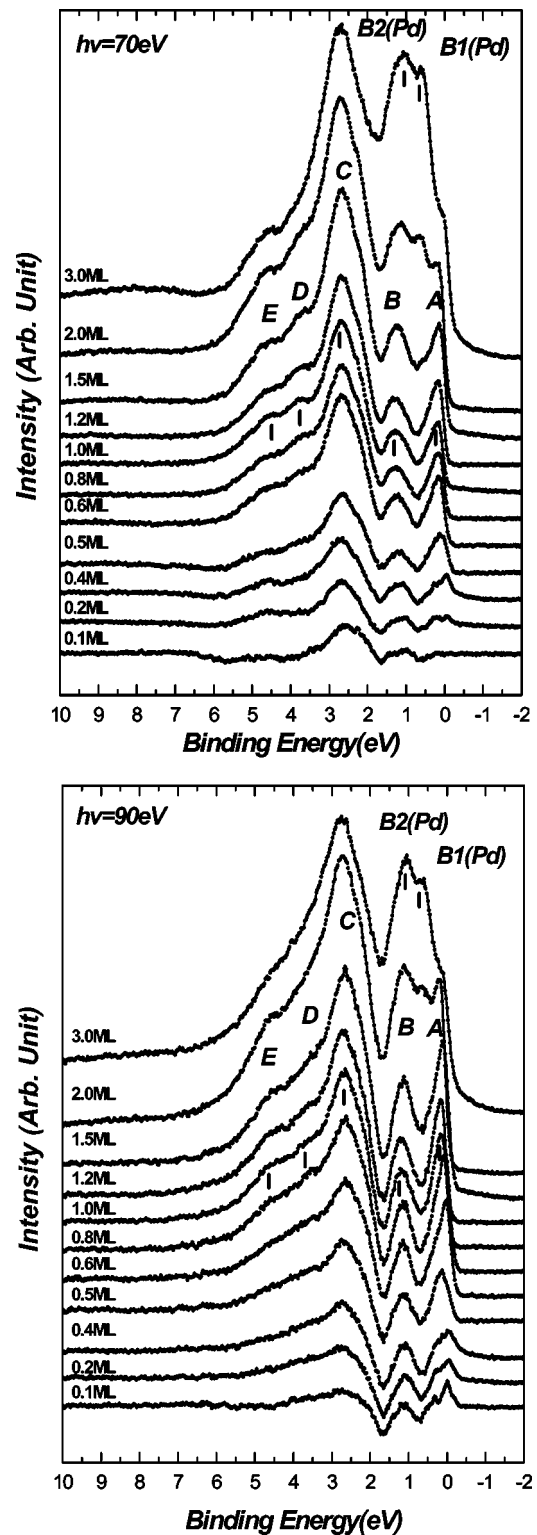


FIG. 4. Valence-band *difference* spectra obtained from the spectra in Fig. 3(a) by subtraction of a scaled spectrum from the clean Re(0001) substrate at 70 eV and 90 eV photon energy.

1.5 ML and higher show strong features of new states denoted B1(Pd) (BE=0.5 eV) and enhanced state B2(Pd) (BE=1.2 eV), which are both characteristic of bulk Pd(111).

As mentioned in the Introduction, Hammer and Nørskov recently developed a powerful model, employing first-

TABLE I. Computed d -band center relative to Fermi level of $[\text{Pd}_{\text{ML}}/\text{Re}(0001) - \text{Re}(0001)]$.

	Experiment at $h\nu=90$ eV	Band-structure calculation (from Ref. [11])
1.0 ML Pd/Re(0001)	2.80 eV	2.70 eV
3.0 ML Pd/Re(0001)	2.46 eV	2.39 eV ^a
d -band shift (Δ)	-0.34 eV	-0.31 eV

^aThe calculated d -band center of the second layer of Pd on Re(0001).

principles density-functional-theory (DFT) calculations, which can predict the chemisorption energy of CO (and H₂) on a large number of transition metals and bimetallic systems of transition metals.⁵ Hammer and Nørskov calculated from first-principles the interaction of adsorbate molecular orbitals with surface metal sp and d bands, and they found that the chemisorption energy can be simply correlated to the position of the metal d -band center from the Fermi level, i.e., the farther away the d -band center is from the Fermi edge, the weaker is the bonding. While Hammer and Nørskov have shown that the model predicts both absolute values of chemisorption energies for specific metal surfaces and trends in energies with the position of the metal d -band center in the Periodic Table that are in excellent agreement with experiment, we are not aware of any experimental verification of the d -band center “metric” in these models. To test this aspect of the model with our experimental result, we calculated the experimental values of the d -band centers from *difference* spectra of 1.0 ML Pd/Re(0001) and 3.0 ML Pd/Re(0001) surfaces using the mathematical definition used by Hammer and Nørskov¹⁴ and compared them to the values from the gradient-corrected DFT periodic slab calculation of Pallassana *et al.*⁶ The comparison is shown in Table I, and the agreement is excellent, particularly in the shift of the d -band center from the Fermi level for the 2D layer at the interface relative to the multilayer.

In Fig. 5, the Pd 1 ML and 3 ML *difference* spectra are plotted together with the DOS of the Pd interfacial layer (slab) in the periodic slab calculation.⁶ First, in a qualitative comparison of peak positions, it is clear that there is excellent agreement with all the major peak positions in the DOS that can be clearly identified in the difference spectra of 1.0 ML Pd/Re(0001), except for the state at BE=2.0 eV. In the case of 3.0 ML Pd/Re(0001), the evolution of the peaks at BE=0.5–1.0 eV and the movement of the d -band center toward the Fermi level from addition of Pd overlayers can be clearly seen. Also, the comparison with the slab calculation reiterates the point made earlier that the experimental features on the high binding side of the valence band, $C-E$, represent the electronic states that are the most unique to the 2D Pd interfacial layer.

In summary, we find that there is a shift to higher binding energy for both the Pd $3d_{5/2}$ core level and the Pd valence band for a Pd monolayer at the Re(0001) interface versus a Pd(111) surface layer. Usually, such a core-level chemical shift is interpreted as arising from charge transfer between the adlayer and the substrate atoms, in this case from Pd to

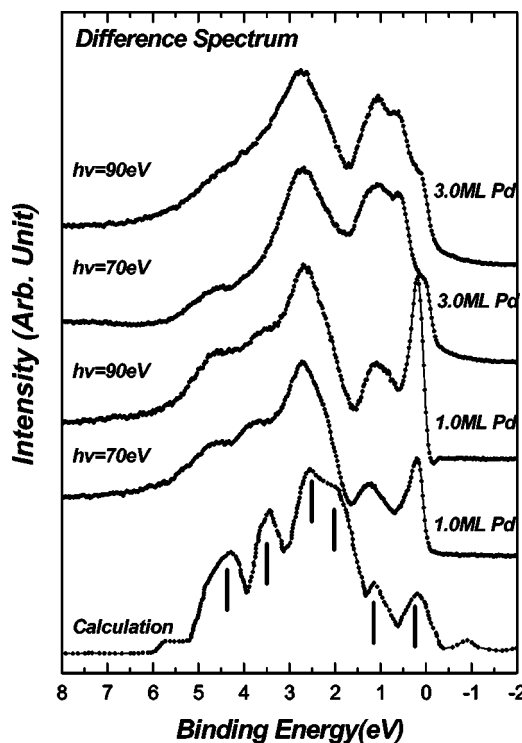


FIG. 5. The *difference* spectra for Pd 1 ML and 3 ML are plotted together with the theoretical band structure calculated DOS for the 2D Pd layer on Re(0001) (Ref. [6]).

Re.³ But the shift in the valence-band DOS away from the Fermi level would usually be interpreted as a “band-filling” charge transfer, i.e., donation of d electron charge by Re to Pd. While the electronic-structure calculations of both Pallassana *et al.*⁶ and Wu and Freeman⁴ indicate that rehybridization of the d bands of both metals is responsible for these chemical shifts, the calculated valence charge-density maps of Wu and Freeman present a clearer physical picture of the charge redistribution accompanying this rehybridization. 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 (thus causing the Pd core-level shift to higher binding energy). On average, the center of negative charge of the Pd layer shifts downward to the substrate, and forms a potential barrier in the interfacial region that lowers the energy of the d valence electrons (thus shifting the d -band center away from the Fermi level). Pallassana *et al.*⁶ pointed out that the d electron count in the Pd interfacial layer was the same as that in a Pd(111) surface layer, i.e., there is no “band filling” by electron donation from the substrate. Rather, the correct physical picture for the electronic modification is substrate-induced charge polarization in the Pd layer.

CONCLUSION

The electronic structure of the Pd/Re(0001) bimetallic surface was investigated as a function of Pd coverage using high-resolution photoemission spectroscopy with a synchrotron radiation source. As the Pd coverage increased, both Pd

3*d* core-level spectra and 4*d* valence-band spectra show unique features attributed to interaction with the substrate, i.e., a positive ACLS and shift of the *d*-band center away from the Fermi level. The magnitude of the shift of the *d*-band center for 1 ML Pd/Re(0001) is in quantitative agreement with the recent DFT periodic slab calculations of Norskov and co-workers. It is possible to reconcile the seemingly contradictory core-level and valence-band shifts based on the charge-density maps from the earlier full-potential linearized augmented-plane-wave band-structure calculation by Wu and Freeman. 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 (thus causing the Pd

core-level shift to higher binding energy). On average, the center of negative charge of the Pd layer shifts downward to the substrate, and forms a potential barrier in the interfacial region that lowers the energy of the *d* valence electrons (thus shifting the *d*-band center away from the Fermi level).

ACKNOWLEDGMENTS

We would like to thank to Professor Charles S. Fadley and Professor Jens Onsgaard for invaluable discussions. This research was supported by the Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

-
- ¹M. W. Ruckman and M. Strongin, *Acc. Chem. Res.* **27**, 250 (1994); M. W. Ruckman and M. Strongin, *Phys. Rev. B* **29**, 7105 (1984); A. Sellidj and B. E. Koel, *ibid.* **49**, 8367 (1994).
- ²D. E. Eastman and W. D. Grobman, *Phys. Rev. Lett.* **30**, 177 (1973); G. K. Wertheim, S. B. DiCenzo, and D. N. E. Buchanan, *Phys. Rev. B* **33**, 5384 (1986); Shigemi Kohiki and Shigero Ikeda, *ibid.* **34**, 3786 (1986).
- ³J. A. Rodriguez and D. W. Goodman, *Science* **257**, 897 (1992); R. A. Campbell, J. A. Rodriguez, and D. W. Goodman, *Phys. Rev. B* **46**, 7077 (1992).
- ⁴R. Wu and A. J. Freeman, *Phys. Rev. B* **52**, 12 419 (1995).
- ⁵B. Hammer, Y. Morikawa, and J. K. Nørskov, *Phys. Rev. Lett.* **76**, 2141 (1996).
- ⁶V. Pallassana, M. Neurock, L. B. Hansen, B. Hammer, and J. K. Nørskov, *Phys. Rev. B* **60**, 6146 (1999).
- ⁷Hussain, Z., T. Huff, S. A. Kellar, E. Moler, P. A. Heimann, W. R. McKinney, C. Cummings, T. Lauritzen, P. McKean, J. Palomares, H. Wu, Y. Zheng, A. T. Young, H. A. Padmore, C. S. Fadley, and D. A. Shirley, *Rev. Sci. Instrum.* **69**, 9 (1995).
- ⁸D. Hennig, M. V. Ganduglia-Pirovano, and M. Scheffler, *Phys. Rev. B* **53**, 10 344 (1996).
- ⁹J. N. Andersen, D. Hennig, E. Lundgren, M. Methfessel, R. Nyholm, and M. Scheffler, *Phys. Rev. B* **50**, 17 525 (1994). R. Nyholm *et al.*, *J. Phys.: Condens. Matter* **4**, 277 (1992).
- ¹⁰C. J. Powell and A. Jablonski, *NIST Electron Inelastic-Mean-Free-Path Database—Version 1.1* (National Institute of Standards and Technology, Gaithersburg, MD, 2000).
- ¹¹I. N. Stranski and L. Krastanov, *Sitzungsber. Akad. Wiss. Wien, Math.-Naturwiss. Kl., Abt. 2B* **146**, 797 (1938).
- ¹²L. F. Mattheiss, *Phys. Rev.* **151**, 450 (1966).
- ¹³F. J. Himpsel and D. E. Eastman, *Phys. Rev. B* **18**, 5236 (1978); H. Chen, N. E. Brener, and J. Callaway, *Phys. Rev. B* **40**, 1443 (1989); J.-S. Kang *et al.*, *J. Magn. Magn. Mater.* **150**, 323 (1995).
- ¹⁴The position of the *d*-band center (first moment) is defined as μ_1/μ_0 , where $\mu_p = \int N(\epsilon)\epsilon^p d\epsilon$. [$N(\epsilon)$ is the DOS and p is the order of moment.]