Core-level spectroscopy of the Pd/W(110) interface: Evidence of long-range Pd-island–W interactions at submonolayer Pd coverages ☆

D.M. Riffe [a,*], N.D. Shinn [b], B. Kim [c,d], K.J. Kim [e], T.-H. Kang [d]

[a] Department of Physics, Utah State University, Logan, UT 84322-4415, USA
[b] Sandia National Laboratories, Albuquerque, NM 87185, USA
[c] Department of Physics, POSTECH, Pohang, Kyungbuk 790-784, Republic of Korea
[d] Beamline Research Division, Pohang Accelerator Laboratory (PAL), Pohang, Kyungbuk 790-784, Republic of Korea
[e] Department of Physics, Konkuk University, Seoul 143-701, Republic of Korea

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ABSTRACT

We have measured W $4f_{7/2}$ core-level photoemission spectra from W(110) in the presence of Pd overlayers for coverages up to ~1 pseudomorphic monolayer (ML). At coverages close to 0.05 ML a striking change in the W core-level spectrum is observed, which we interpret as indicating a long-range lateral effect of 2D Pd islands upon the W electronic structure in both the first and second W layers. As the coverage increases the long-range effect weakens and finally vanishes near 0.85 ML. Above this coverage the W spectra are typical for a W-based bimetallic interface, with the first-layer W atoms exhibiting a small interfacial core-level shift (-95 ± 5 meV) compared to the bulk atoms.

1. Introduction

The study of bimetallic interfaces has long been driven by the possibility of tailoring surface electronic properties for chemical, catalytic, and electronics applications. Atomic intermixing at the interface can, of course, lead to new and unexpected electronic structure [1,2]. However, novel surface electronic properties can result in systems with no intermixing. For example, the electronic structure of ultrathin Pd films on transition-metal substrates varies systematically with the substrate across the periodic table [2–7]. In fact, for Pd grown on bcc(110) metal surfaces (Nb, Ta, Mo, and W) the electronic structure of monolayer, pseudomorphic Pd most closely resembles that of a noble metal [2,8–12], leading to surface chemical properties that are very different than those at the surface of bulk Pd [2,4,13–24]. Clearly, a surface atom's properties can be substantially influenced by its bonding with the underlying substrate.

Conversely, an ultrathin metallic overlayer can affect the underlying substrate. This is most dramatically illustrated in the phe-

nomenon of overlayer-induced faceting of bcc(111) surfaces (Ta, Mo, and W) [25–36]. Recently, more subtle overlayer-induced effects have been investigated. For example, studies of overlayer mesoscopic islands show that an island can induce substantial elastic strain in the surrounding substrate atoms [37–39]. These island-induced strains can influence adatom diffusion [40,41], which can subsequently impact island growth and morphology. Overlayer islands can also influence adatom diffusion through their interaction with electrons in substrate surface states [42–44]. These observations naturally raise the following question: can mesoscopic islands produce significant changes in the electronic structure of the surrounding substrate surface atoms? If so, such an effect might be important to the overall chemical, catalytic, or electronic behavior of the interface.

Here we present evidence that mesoscopic islands can, indeed, significantly alter the electronic structure of nearby substrate surface atoms. Our evidence consists of substantial changes in the core-level spectrum of W(110) upon deposition of very low Pd coverages. The data indicate that the range of the affected W atoms extends ~1 nm from the Pd-island edges. Consideration of this range, the magnitude of the core-level shifts (~100 meV), and the coverage dependence of the shifted components leads us to surmise that the Pd islands induce a reconstruction in the region surrounding each island. Furthermore, consideration of earlier very-low-coverage Re/W(110) core-level data [45], which are essentially identical to the data presented here, indicates that this

phenomenon is not unique to Pd/W(110); it may thus be a more general phenomenon associated with bimetallic-island formation on W(110) and possibly other bcc(110) surfaces.

2. Experimental details

The W $4f_{7/2}$ spectra were obtained using beamline U4A at the National Synchrotron Light Source, which includes a 6-m torodial-grating monochromator and an end station with a 100-mm hemispherical electron-energy analyzer. The data were obtained using 70 eV photons at a total (photon plus electron) energy resolution of ~125 meV.

The W crystal was cleaned by the standard technique of sample annealing at 1550 K in an oxygen environment with periodic flashes to 2400 K [46]. As discussed in detail below, cleanliness is assessed via W $4f_{7/2}$ photoemission spectra from a freshly flashed sample. We estimate surface contamination to be <1% of a monolayer (ML). The Pd layers were deposited on the room temperature W surface from a shuttered evaporator surrounded by a liquid-nitrogen-cooled shroud. Typical adsorption rates were on the order of 0.05 ML/min.

3. Results and analysis

The data in Fig. 1 illustrate the development of the W $4f_{7/2}$ spectrum with increasing Pd coverage, determined as described in Section 4.2. The top curve, from a clean surface, consists of two peaks: the lower binding energy (BE) peak (surface) is from W atoms in the first atomic layer, and the higher BE peak (bulk) is from W atoms in the second atomic layer and deeper [47,48]. The solid and dashed vertical lines mark the BE's of the bulk and clean-surface atoms, respectively. At the lowest Pd coverages in our study
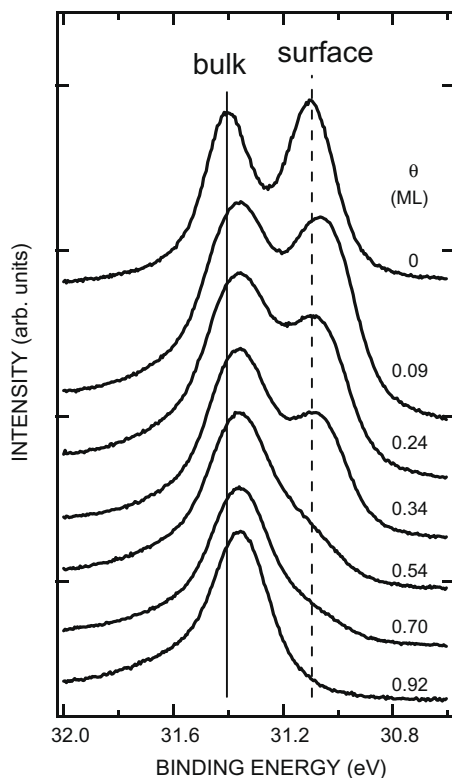

Fig. 1. W $4f_{7/2}$ core-level spectra from the Pd/W(110) bimetallic interface, illustrating the effect of increasing Pd coverage. The solid and dashed lines mark the positions of the bulk and clean-surface core-level features, respectively.

(~0.05 ML), the spectrum undergoes a remarkable change: both peaks in the spectrum shift to lower binding energy and become significantly broader. This is in marked contrast to the change induced by low coverages of Ni or Pt, for example, which simply cause the low BE peak to decrease in height and move to higher BE [49,50]. With further coverage, however, the spectrum does becomes more typical of a late transition-metal overlayer on W: the lower BE peak diminishes in size until only one peak is visible [49,51,52]. As in the case of Ni deposition on W(110), this single peak is at a slightly lower BE than the bulk peak, indicating that the Pd influenced atoms have a BE that is slightly lower than the bulk-atom BE [49].

We use least-squares fitting to decompose the core-level data into spectral components. Each W $4f$ core-level photoemission feature is modeled by a Gaussian broadened Doniach–Šunjić (DS) peak [48,53], which is described by five parameters: a Lorentzian width, singularity index, binding energy, peak height, and Gaussian width. We use a linear function to describe the background.

Fig. 2a illustrates a least-squares fit to a spectrum from the W(110) surface before Pd deposition. The fit is dominated by two DS components (labeled B and S) that have parameters consistent with data obtained at higher resolution [48]. Additionally, in order to get a satisfactory least-squares fit to the spectrum it is necessary to include two more, much smaller components, as illustrated. As recently discussed in our core-level study of Ni/W(110), the higher binding-energy component is likely from residual C on the surface [49]. Given the size of this peak (2.1 ± 0.2% of the surface $4f_{7/2}$ peak) and the expectation that C sits in the quasi-three-fold hollow site, the contamination is estimated to be <1% of a ML. The small peak that sits between the bulk and surface peaks is possibly due to step-edge atoms on the surface [54,55].

At lower Pd coverages satisfactory fits to the spectra can only be obtained by adding in two more core-level components (I_1 and I_2), as illustrated in Fig. 2b–d. The presence of these two components is responsible for the initial shift and broadening of the W $4f_{7/2}$ spectrum. The need for both of these interfacial components is independent of the exact details of the least-squares analysis.

However, because the Pd induced components are not resolved, it is necessary to limit the number of free parameters in the analysis in order to obtain physically reasonable results over the whole range of Pd coverages. We initially constrained the fitting parameters to values obtained from clean-surface spectra, and subsequently relaxed the constraints, as necessary, until a satisfactory fit is obtained. For example, the BE's of the B and S components were initially maintained at their clean-surface value. This constraint is satisfactory at coverages <~0.5 ML, but acceptable fits at higher coverages can only be obtained if the S peak is allowed to move to slightly higher BE, as illustrated in Fig. 2d–f. Similar considerations were applied to the parameters that describe the components' shape. For example, the B and S lines of the clean-surface spectrum have nearly identical Gaussian widths. We thus constrained the Gaussian width of all lines to be identical, and satisfactory fits for all Pd coverages were obtained with this constraint. Because the I_1 and I_2 peaks are associated with first and second layer W, respectively (see Section 4.1), we also fixed their Lorentzian widths to equal those of the S and B peaks. However, we found that satisfactory fits could only be obtained by allowing the Lorentzian width of the I_1 peak to become slightly smaller. For as-deposited Pd we also found it necessary to allow the singularity index of all of the lines to increase compared to the clean-surface values. This increase can be ascribed to an asymmetric inhomogeneous broadening of the core-level components and/or a Pd induced change in the screening character of the core holes.

With these constraints the least-squares analysis provides following insights into the spectra from the Pd covered surface. As Fig. 2 illustrates, with increasing Pd coverage (beyond our lowest