# Interface Structures of Ordered Fe and Gd Overlayers on W(110) from Site-Specific Photoelectron Diffraction

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## INTRODUCTION

A key advantage of photoelectron diffraction (PD) as a surface structure probe is in permitting state-resolved or site-specific structural determinations via core level binding energy shifts [1]. This method has not been applied previously to metal-metal interfaces, and we here report site-specific and full-solid-angle photoelectron diffraction data from interface W atoms just beneath ordered (1x1) Fe and (7x14) Gd monolayers on W(110) [3]. These data were obtained by utilizing core level shifts in the W $4f_{7/2}$ spectrum. Shinn et al. [3] first observed interface core-level shifts (ICLS's) in W $4f_{7/2}$ photoelectron spectra from W(110) surfaces covered with one monolayer (ML) of Ni, Pt, or Fe in pseudomorphic (1x1) structures. In the case of (1x1) Fe, the W $4f_{7/2}$ spectrum consists of three components: one from the interfacial W layer shifted by -225 meV from the bulk position, another from what appears to be the second W layer shifted by -80 meV, and a third from the bulk W atoms situated below (which is found to remain at the same distance from the Fermi level as for the clean surface) [3]. In this study, we have examined both the pseudomorphic (1x1) Fe monolayer on W(110) [3] and the non-pseudomorphic (7x14) Gd monolayer on W(110), which forms a Moiré pattern with long-range order [4]. Comparison of our experimental data with multiple scattering calculations permits determining the Fe adsorption site and the relative interlayer spacing to the first and second W layers [2]. These Fe results are also compared to those from the very different Gd overlayer and from the clean W(110) surface which has recently been studied by Ynzunza et al. as a reference case [5].

## EXPERIMENT

The PD measurements were performed with the advanced photoelectron spectrometer/diffractometer [6] situated on bend magnet beamline 9.3.2 of the ALS [7]. This system couples a high-resolution spherical grating monochromator to a high-resolution/high-luminosity Scienta SES-200 analyzer, and it is possible with it to acquire individual photoelectron W $4f_{7/2}$ spectra with both excellent statistics (~40,000 peak counts) and resolution ($\leq$80 meV) in the short data acquisition times (~40 s/spectrum) required for large-scale PD measurements.

## RESULTS

The W $4f_{7/2}$ photoelectron spectra for the clean W(110) surface, the (1x1) Fe-covered surface, and the (7x14) Gd-covered surface are shown in Figs. 1(a), (b), and (c), respectively. All of these spectra were obtained with $\theta = 45^\circ$ as measured with respect to the surface and with $\phi$ pointing along the W [001] direction in the sample plane ($\phi = 90^{\mathrm{o}}$ in our notation). For each of the three spectra, there exist two prominent peaks, one at higher $E_b$ corresponding to emission from the bulk W atoms (or 2nd layer W atoms for the (1x1) Fe-covered surface) and a second at lower $E_b$ due to emission solely from the top layer of W atoms (which can be at the free surface or at the metal-metal interface). In the case of the Fe or Gd covered surface, the PD effects associated with this lower $E_b$ feature thus allow us to probe directly the local environment of the W atoms at the interface. The clean W(110) surface shift is measured to be -320 meV, while the ICLS's for the (1x1) Fe covered surface are -235 meV and -90 meV for the interface and the 2nd layer, respectively, in excellent agreement with prior measurements [3]. The ICLS for (7x14) Gd is -390 meV, a noteworthy result because this is the largest shift yet observed for surface or metal-metal interface atoms on W(110).

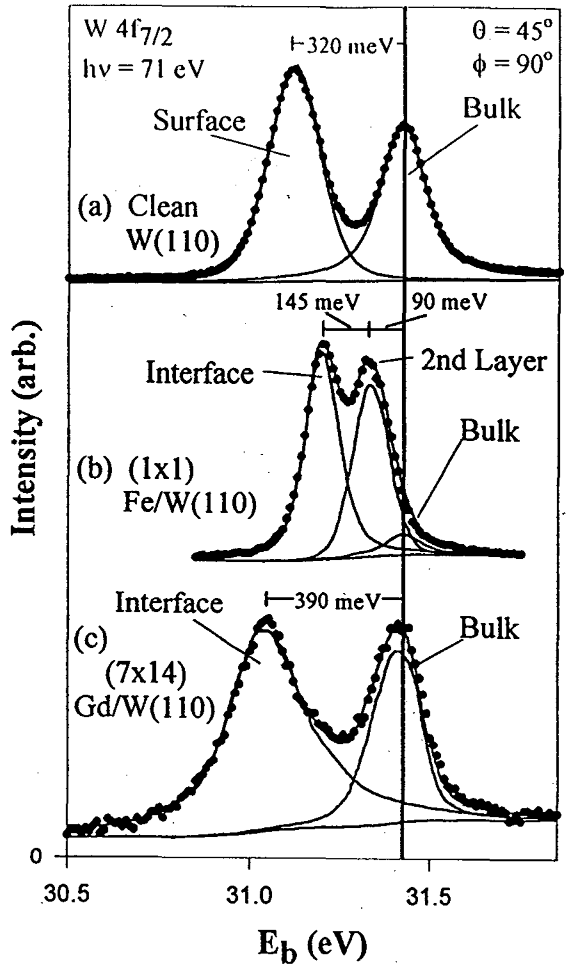

**Figure 1. W $4f_{7/2}$ photoelectron spectra taken with hν = 71 eV, $\theta = 45^\circ$, and $\phi$ along the W [001] azimuth from (a) the clean W(110) surface, (b) 1.2 ML of Fe in a(1x1) overlayer on W(110), and (c) 1.2 ML of Gd in a (7x14) Moiré structure on W(110).**

Considering first the Gd overlayer, we note that prior STM and LEED results show that it consists of a hexagonal overlayer which is very close to Gd(0001) in atomic arrangement, with only a 1.2% expansion along W[001] and a 0.6% contraction along W[-110]. The resulting Moiré pattern or coincidence lattice forces the Gd into 24 different adsorption sites and leaves the underlying W interface atoms largely undercoordinated in 32 inequivalent emitter sites. Thus, the Gd to first order looks like a loosely bound overlayer capable of screening the core hole formed in W 4f emission, and this qualitatively explains the decrease in binding energy of the interface W atoms relative to the clean-surface W atoms. In addition, the multiplicity of adsorption sites and emitter types means that the Gd overlayer acts as a source of more or less diffuse background scattering, as far as the interface and bulk W atoms are concerned. Therefore, the W PD patterns with the Gd overlayer are not expected to be very different from those of the clean surface, and this is in fact what we observe. Figs. 2(a),(c),(f), and (g) show some individual azimuthal diffraction data which illustrate this point.

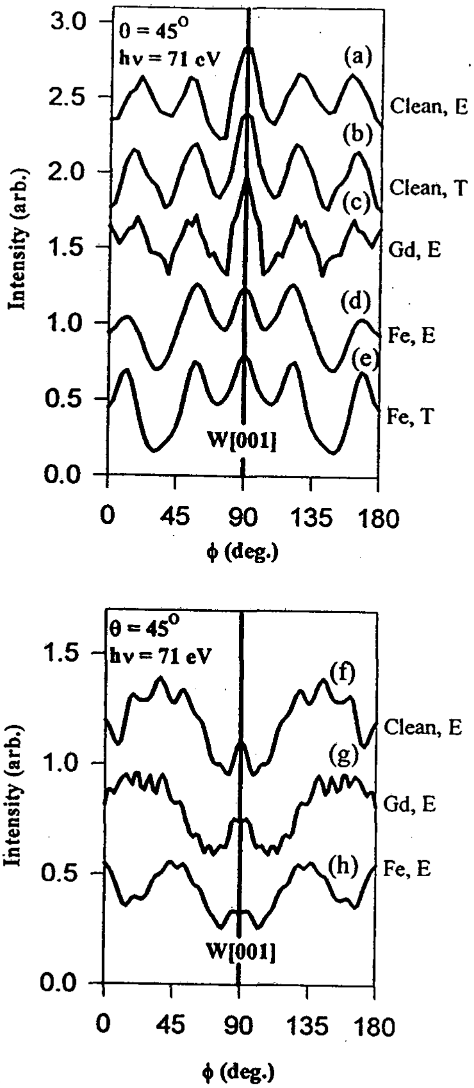

**Figure 2.** Single W $4f_{7/2}$ azimuthal scans taken with hν = 71 eV, and θ = 45° from (a) experiment for the -320 meV-shifted clean-surface peak; (b) theory for the clean surface peak in (a) (from ref. 4); (c) experiment for the -390 meV-shifted interface peak of (7x14) Gd/W(110); (d) experiment for the -225 meV-shifted interface peak of (1x1) Fe/W(110); (e) theory for the Fe/W case in (d), with Fe at the optimum positions in the twofold bridge site; (f) experiment for the clean W(110) bulk peak; (g) experiment for the bulk peak of (7x14) Gd/W(110); and (h) experiment for the 2nd layer peak of (1x1) Fe/W(110).

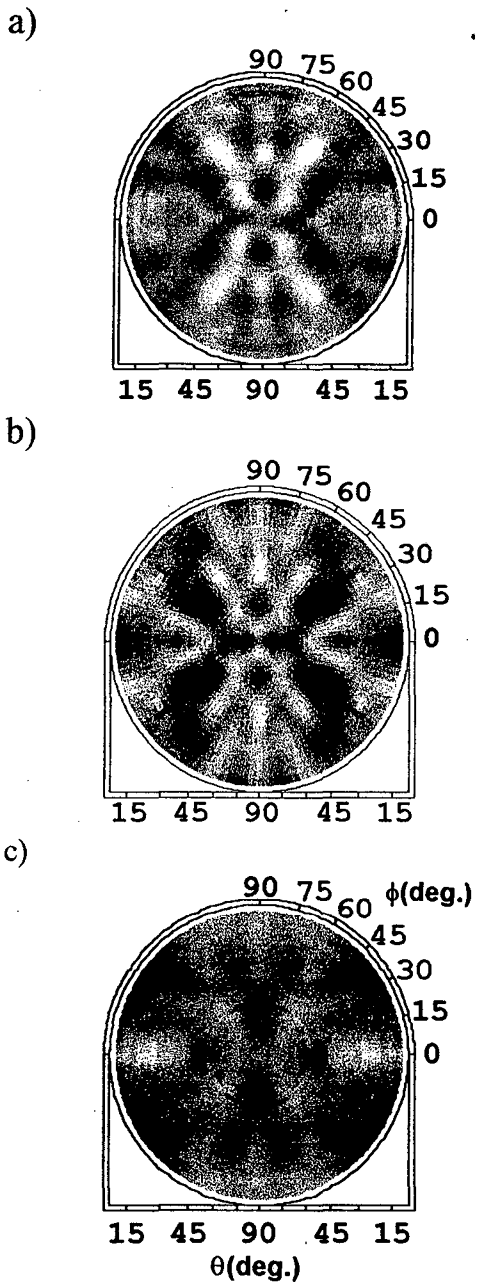

**Figure 3.** Full-solid-angle W $4f_{7/2}$ PD patterns for the (1x1) Fe/W(110) system taken from (a) experimental data for the -235 meV-shifted W interface peak, (b) theoretical multiple scattering calculations for the (1x1) Fe/W(110) interface with an optimized twofold bridge adsorption site for the Fe, and (c) experimental data for the -90 meV-shifted W 2nd-layer peak. The photoelectron kinetic energy outside the surface was $E_k$ = 40 eV in all cases. The data shown span takeoff angles relative to the surface from 12° to 90°(normal emission), and the W(100) azimuth is toward the top of the page in each of these stereographic projections.

For the Fe overlayer however, the W atoms all have a definite coordination to the Fe, and the strength of the bond formed is illustrated by the considerable perturbation of both the interface and the second-layer W binding energies, as shown in Figs. 1(a) and (b). Full-solid-angle PD patterns were measured for this overlayer for both the interface and second-layer peak, and Figs. 3(a) and 3(c) show our results for these two cases, respectively. These data were analyzed by using R-factors to compare them to multiple scattering calculations for different atomic geometries in which both the Fe-W interface vertical distance ($z_{12}$) and the distance between the interface and second-layer W atoms ($z_{23}$) were varied to achieve the best fit to experiment. The best fit was found for Fe sitting in a two-fold bridge site which is equivalent to continuing the bulk W structure, with a distance $z_{12} = 2.17$ Å and a $z_{23}$ corresponding to a slight expansion (~0.05 Å) relative to bulk W. The theoretical diffraction pattern for this optimized geometry is shown in Fig. 3(b).

## CONCLUSIONS

The structure of a metal-metal interface ((1x1) Fe on W(110)) has thus been determined quantitatively for the first time by means of site-specific photoelectron diffraction. This study thus opens up the possibility of using such high-resolution site-specific photoelectron diffraction to study a variety of metal-metal interface systems.

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