Full-Solid-Angle Photoelectron Diffraction from Bulk and Surface Atoms of Clean W(110)

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INTRODUCTION

We have studied the atomic structure of the clean W(110) surface by means of site-resolved scanned-angle W4$f_{7/2}$ photoelectron diffraction (PD) data obtained over nearly the full 2π solid angle above the surface. Prior to the availability of high-brightness sources such as the Advanced Light Source, such large high-resolution data sets were prohibitively time consuming to obtain. The well characterized W(110) system [1-5] was used as a reference case to check the accuracy of structure deteminations from such scanned-angle data via R-factor comparisons of experiment with theoretical multiple scattering calculations. The photoelectron kinetic energy of ~40 eV used was also lower than in many prior PD studies, providing further challenges to theory. The influence of various non-structural theoretical input parameters (e.g., scattering phase shifts, electron inelastic attenuation length, and inner potential) was thus also assessed. A final optimized structure is presented, together with comments on the future applications of this method.

EXPERIMENT

These experiments were performed on bend-magnet beamline 9.3.2 at the ALS [6(a)] using its advanced photoelectron spectrometer/diffractometer experimental station [6(b)].

The sample was prepared by an initial oxygen reduction at a temperature of 1200°C and a pressure of $1x10^{-7}$ torr O_2 to reduce the amount of carbon from the near-surface region. This was followed by repeated flashing at up to 2200 °C by electron bombardment heating. Sample cleanliness was then monitored by x-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), and most sensitively by the surface core level shift (SCLS) between the bulk and surface atoms, which reaches a maximum value of ~320 meV for a fully clean surface [1(b)]. Fig. 1 shows (a) the schematic experimental geometry and (b) a typical spectrum. For a given sample preparation, the actual data collection time was limited to 30 minutes to maintain adequate cleanliness. The base pressure during measurements was $1.3x10^{-10}$ torr.

The photoelectrons were excited by 70 eV linear-polarized light from a spherical-grating monochromator [6(a)]. This resulted in W 4$f_{7/2}$ photoelectrons at a kinetic energy of ~39-40 eV, as shown in Fig. 1(b). The angle between the incident radiation and the analyzer (which is in fact variable for this system [6(b)]), was for this experiment fixed at 70°. To enable the most accurate measurement of the bulk and surface peak intensities, individual spectra were obtained at each direction and stored for later analysis by peak fitting. Data were obtained over the nearly full 2π

solid angle above the surface by rotating the sample on two perpendicular axes for polar takeoff angle θ and azimuthal angle ϕ. The data consisted of twenty-eight azimuthal scans spanning takeoff angles with respect to the surface from 9° to 90° (=normal emission) and with 3° steps in takeoff angle. The azimuthal step size was adjusted with takeoff angle such that the final data set consisted of 892 spectra representing roughly equal solid-angle increments. Angles below 9° were not used due to the much lower count rates and thus longer counting times involved. Due to the symmetry of the crystal surface, only a 90° azimuthal scan is in principle needed to provide information on the full 360° intensity profile. However, to increase accuracy and average over any small sample misalignments, we collected data over 180° in azimuth, and then mirror-averaged this into a 90° sector that was finally used to generate full 360° representations of our data. At each direction, a W $4f_{7/2}$ photoelectron spectra was taken with a Scienta SES 200 hemispherical electrostatic spectrometer [6(b)]; the high luminousity of this spectrometer permitted taking a single high-resolution spectrum in ~20 seconds. Any variations of radiation flux with time were normalized out in determining the final intensities.

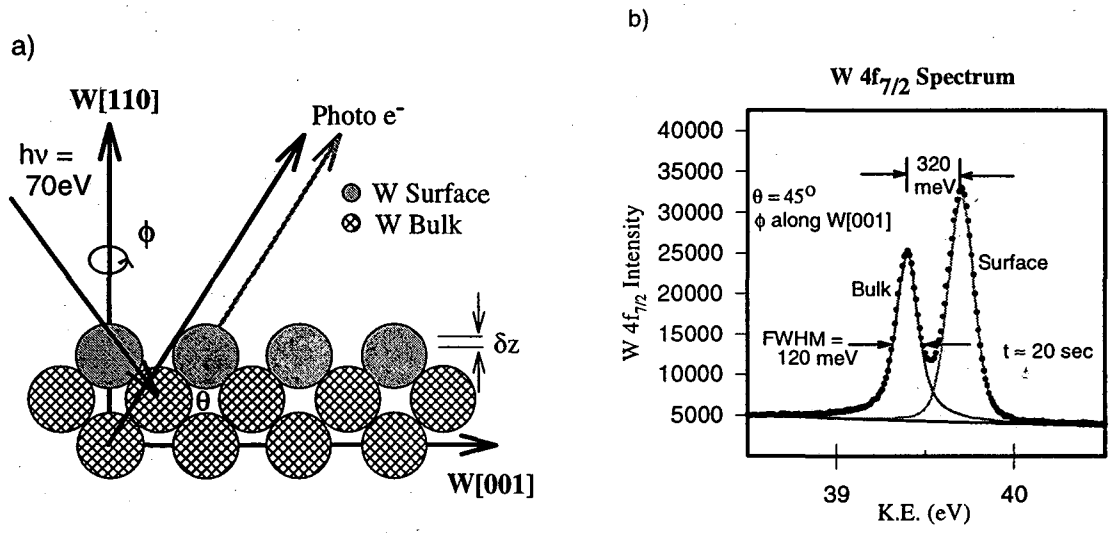

Figure 1. (a) A schematic of the experimental geometry, showing the two types of tungsten atom sites studied. (b) A W $4f_{7/2}$ photoelectron spectrum, showing the two component due to bulk atoms and surface atoms, with a surface core level shift (SCLC) between the two of 320 meV. Emission was at a takeoff angle with respect to the surface of $\theta = 45^{o}$ and an azimuthal angle of $\phi = 90^{o}$ (lying along the [100] direction in the W(110) surface).

RESULTS

The easily resolvable surface core level shift in Fig. 1(b) permits deriving site-specific photoelectron diffraction patterns from both the tungsten atoms in the surface layer and the tungsten atoms below the surface layer. The 39-40 eV kinetic energy range of the photoelectrons is also very near the minimum in their inelastic attenuation length, which we have estimated from an analysis of the takeoff-angle dependence of the surface/bulk intensity ratio [7] to be only 3.0-4.0 Å. This very small value enhances the surface contribution, making it stronger than that for the bulk in many emission directions, as illustrated in Fig. 1(b). Due to the different local

geometry around the two types of atoms, the bulk and the surface diffraction patterns are also strikingly different, as seen in the full-solid-angle patterns presented in Figs. 2(a),(c).

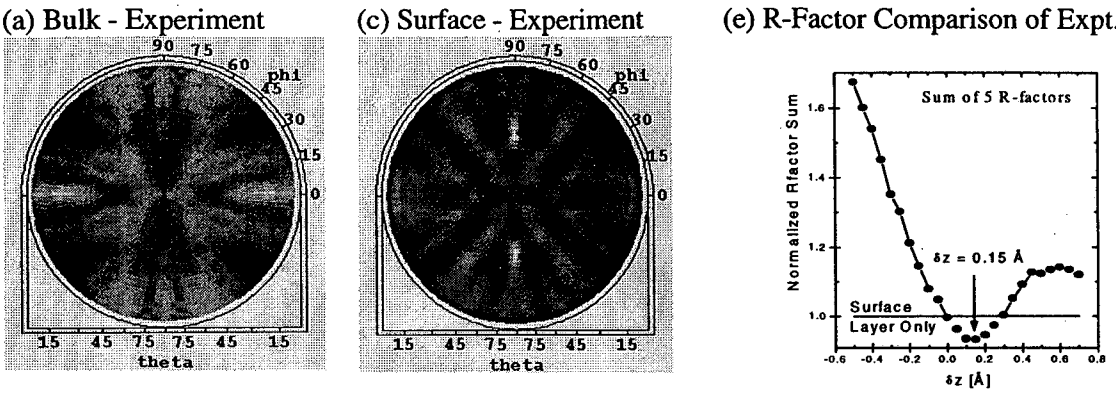

Figure 2. Full-solid-angle W4f$_{7/2}$ photoelectron diffraction patterns: (a) bulk-resolved experiment, (b) bulk theory for the optimum interlayer distance, (c) surface-resolved experiment, and (d) surface theory for the optimum interlayer distance. (e) R-factor comparison between experiment and multiple-scattering theory for the surface-atom W 4f$_{7/2}$ photoelectron diffraction pattern of Fig. 2(b). The curve represents a normalized sum of five R-factors defined in ref. 10(b). The horizontal line corresponds to an R-factor for calculations in which no bulk scatterers were present.

Multiple scattering diffraction calculations were performed using a program developed by Chen et. al. [8] and based on the previously-used Rehr-Albers approximation for treating the multiple scattering of photoelectrons [9]. Because of its high atomic number, tungsten is a very strong scatterer, particularly for low-energy electrons [9b]. Thus, several different sets of calculated scattering phase shifts were tried, along with variations in other non-structural parameters such as the electron attenuation length and the inner potential. Experiment was compared to theory via a set of 5 R-factors originally suggested for LEED analyses [10(a)] and later modified for PD analyses [10(b)]. The trial atomic geometries in theory involved a series of outward relaxations or inward contractions of the surface layer with respect to the second layer below, with the relevant distance being defined as δz (measured relative to the unrelaxed bulk interlayer distance). Fig. 2(e) shows the variation of a normalized sum of these five R-factors with δz. All five R factors are found to yield very nearly the same structure, with the overall conclusion being a small 0.15 ± 0.05 Å outward relaxation of the surface layer from its normal bulk termination. This is thus 6.7% of the bulk interlayer distance of 2.23 Å. The excellent final agreement between experiment and theory for surface emission is illustrated in Figs. 2(c) and (d). The analogous comparison for bulk emission in Figs. 2(a) and (b) shows good agreement, with further calculations for this more complex multi-layer emission problem still in progress. Another interesting aspect of the surface-atom analysis is that theory and experiment are in general in very good agreement if only the surface layer of scatterers is included in the calculation (i.e., if no bulk scatterers are present); this is represented by the horizontal line in Fig. 2(e). However, with a proper calculation including all scatterers, the influence of the bulk scatterers is evident: the minimum R-factors are slightly lower for the optimum geometry, and the values for interlayer distances more than about 0.7 Å away

from the optimum are significantly higher, such that the agreement decreases. Our final structural conclusion for this structure agrees with prior PD results by Jugnet et al. based on a much smaller data set , which show no relaxation to within ± 0.2Å [2]. Our structure is also in general agreement with prior LEED studies of this surface, which have reached conclusions varying from a small contraction of 0.07Å[3] to no relaxation at all [4,5].

CONCLUSIONS

This study thus has applied site-resolved full-solid-angle photoelectron diffraction to the well-defined test case of the clean W(110) surface, for which the surface and bulk diffraction patterns can be measured separately. Multiple scattering theory is found to provide an excellent description of the surface data, even at a low kinetic energy of ~40 eV, and R-factor comparisons of experiment and theory permit deriving structural information with an accuracy of ~±0.05 Å. Future applications of such large-scale site-resolved data sets to various surfaces and interfaces are thus promising.

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