Circular dichroism in core-level emission from O/W(110): Experiment and theory

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Circular dichroism has been observed in the photoelectron diffraction of chemically shifted W $4f$ photoelectrons from the W(110)1×1-O surface. The diffraction peaks from first-layer W atoms bonded most directly to oxygen showed an azimuthal rotation similar to those reported in a prior experiment on Si(001). The maximum rotation angles are also in good agreement with those calculated using the formula $\Delta\phi = m/kR \sin^2\theta$ derived previously by Daimon *et al.* [Jpn. J. Appl. Phys., Part 2 **32**, L1480 (1993)] and assuming $m=4$, which is the maximum magnetic quantum number of the photoelectron wave function. [S0163-1829(98)05139-X]

I. INTRODUCTION

Recently, Daimon *et al.*[1] have observed circular dichroism in photoelectron diffraction patterns from nonchiral and nonmagnetic Si(001). The most pronounced diffraction peaks in the two-dimensional intensity pattern are found to be rotated in the same direction as the direction of rotation of the electric vector of the incident circularly polarized light. The rotation of these peaks has been explained as being due to the transfer of angular momentum to the photoelectron wave function, whose z component angular momentum has been changed by ± 1 in being excited by the circularly polarized light.

These effects in Si have also been well reproduced by multiple scattering diffraction calculations by Kaduwela *et al.*,[2(b)] with the calculations also exhibiting other effects more complex than simple rotations. It has also been pointed out[2] that these effects are closely related to prior studies of adsorbates on metals by Schönhense and co-workers[3] and often termed circular dichroism in angular distributions. It is thus of interest to study this phenomenon on other simpler systems in order to understand it more clearly. In the present study, we have measured circular dichroism in photoelectron diffraction from chemically shifted W $4f$ core levels for the system W(110)1×1-O surface, focusing in particular on the first W layer bonded most directly to oxygen for which a single-scattering diffraction picture should be most applicable.

In a separate paper,[4] we have analyzed the structure of this surface using full-solid-angle chemically shifted W $4f$ x-ray photoelectron diffraction patterns. The resulting two-dimensional pattern from the first-layer W atoms showed strong forward-focusing peaks in the direction of the overlying oxygen atoms. The atomic configuration thus derived is shown schematically in Fig. 1. The forward-focusing peaks from the first-layer oxide W atom in the *A* direction at the typical energies of 317 eV studied here can be considered to be produced mainly by single scattering by the atom along *A*.

II. EXPERIMENT

The experiments were performed at beamline 9.3.2 of the Advanced Light Source at the Lawrence Berkeley National Laboratory.[5] Since this is a bend-magnet beamline, it is pos-
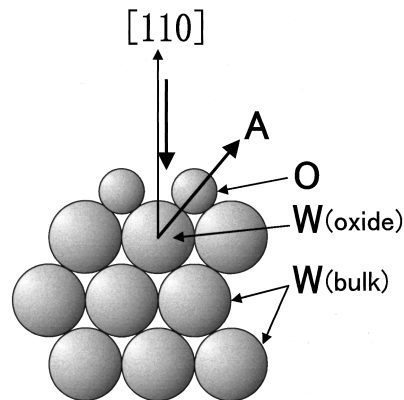

FIG. 1. Experimental configuration used in the present study, including the schematic atomic geometry, as determined more quantitatively in Ref. 4.

sible to obtain both linearly and circularly polarized light simply by accepting different vertical segments of the beam.[6] In the present study, the right and left circular polarization of the light was more than 85%.

The primary analysis chamber is equipped with a Scienta SES200 electron energy analyzer, low-energy electron diffraction (LEED), and x-ray photoelectron spectroscopy (XPS), and is described in more detail elsewhere.[7] The SES200 analyzer can rotate over 55° in the plane of the storage ring via differentially pumped seals. The sample can also be rotated around two axes by computer-controlled motors. The angular resolution can be controlled to ±2° using a collimator. The pass energy was 5 eV, and the total energy resolution was about ~0.1 eV. The base pressure was 1 ×10⁻¹⁰ mbar.

The clean W(110)1×1 surface was obtained by repeated oxidation (1000 L at 300 °C) and annealing (1700 °C, 30 sec) cycles and confirmed by both XPS with a standard Al $K\alpha$ source and by a sharp 1×1 LEED pattern. The W(110)1×1-O surface was made by dosing with oxygen at 3.0×10^{-6} mbar for 1000 sec at a W temperature of 710 °C. This procedure is the same one we used in the previous structural analysis,[4] and the resulting LEED pattern, which has both primitive and (1×12) superstructure spots, is exactly the same as in prior studies.[4,8]

The light was incident perpendicular to the surface, and thus parallel to the [110] direction. The dependence of photoelectron intensity on azimuthal angle was measured by rotating the sample around the [110] direction. The polar take-off angle of the photoelectron (as measured relative to the surface) was changed by rotating the SES200 analyzer. The forward focusing peaks in XPS in Ref. 4 are observed in the polar take-off angle range from 15.0° to 32.0°. In this study we thus measured the azimuthal-angle dependence in the polar-angle range from 16.5° to 29.0°, a range over which we should be able to observe some evidence of forward-focusing peaks. Forward-focusing peaks are much sharper and more evident in XPS than at the lower energies involved in this study. However, the sharpness of the forward-focusing peaks is not essential in this study because we discuss only the rotational shifts of the peak centers, and these shifts should be large enough at lower energies. Also, we will average over polar angles to more clearly see any azimuthal peak shifts.

III. RESULTS

Figure 2 shows W $4f$ spectra from the W(110)1×1-O surface taken with a photon energy of 350 eV and a resulting photoelectron kinetic energy of approximately 317 eV. We can clearly see two pairs of chemically shifted peaks, with two representing ''bulk'' W atoms and two representing W atoms bonded directly to oxygen. The solid curves are fits of analytical peak shapes to the spectra; the shape was a combination of standard peak shapes (asymmetric Lorentzian+Gaussian, and an integral background of the Shirley type). The bulk peaks can be fitted well with two peaks of identical shape and a full width at half maximum (FWHM) of 0.47 eV, separated by the spin-orbit splitting of 2.16 eV, and with an intensity ratio of 1:0.75 that is equal to the occupation ratio of these subshells. The oxide peaks are
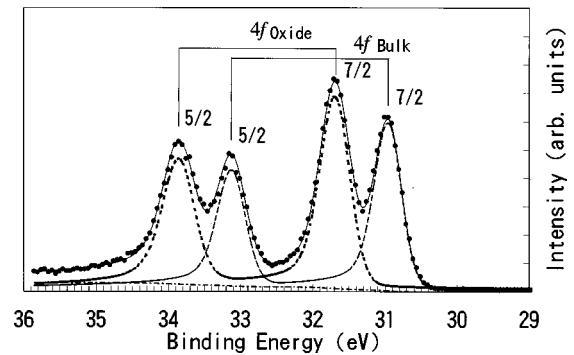

FIG. 2. W $4f$ spectrum from the W(110)1×1-O surface taken with a photon energy of 350 eV, including peak fitting into oxide and bulk components.

also fitted well with peaks of the same shape as that of the bulk peaks, although they are somewhat broader, with a FWHM of 0.51 eV. The peak positions of the oxide peaks are shifted by the charge transfer from W to oxygen, yielding a core-level shift of 0.73 eV, which is the same as that obtained previously by XPS.[4] The fitted curve for the spectrum is the sum of the curves for bulk peaks, oxide peaks, and background.

We measured such chemical-state-resolved spectra using linearly polarized, as well as left circularly polarized light over the polar take-off angle range from 16.5° to 29.0° in 2.5° steps, and over the azimuthal-angle range of 222° in 3° steps. We obtained two-dimensional angular distribution patterns for each component by separating the observed spectra into the bulk and oxide components using curve fitting such as that in Fig. 2. The azimuthal scale was determined using high-symmetry axes in azimuthal diffraction patterns for linearly polarized light.

Figure 3 shows the two-dimensional diffraction pattern from the chemically shifted W $4f$ oxide peak from the first-layer W atoms in the polar take-off angle range from 16.5° to 29.0°. The center of each pattern corresponds to the surface normal direction. The stereographic projection method was used to make these plots. The horizontal direction is [001]. Figures 3(a) and 3(b) show our results for linearly polarized (LP) and left circularly polarized (LCP) light, respectively. Here the definition of LCP is that the rotation direction of the electric vector of the photon as seen by someone riding with the photon (and thus also into the planes of Fig. 3) is counterclockwise (ccw). The patterns for linearly polarized light have been averaged using mirror symmetry with respect
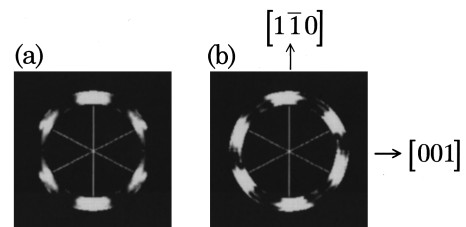

FIG. 3. Two-dimensional diffraction patterns of the chemically shifted W $4f$ oxide peak from the first-layer W atoms over a polar take-off angle range from 16.5° to 29.0°. (a) and (b) show the results for linearly polarized and left circularly polarized (ccw) light, respectively. The white lines show the directions of the forward-focusing peaks observed using linearly polarized light.
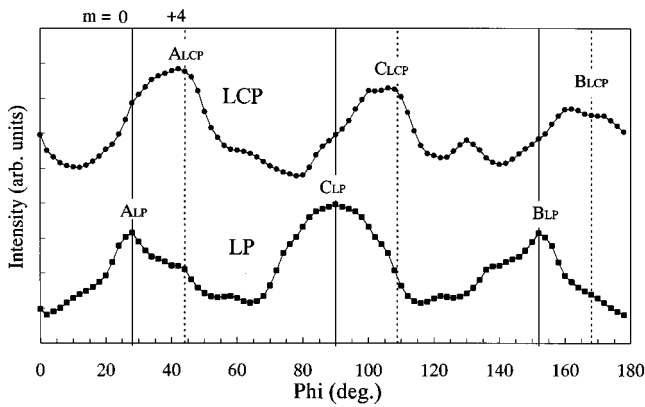
FIG. 4. The azimuthal dependence of the W $4f$ oxide peak intensity in Fig. 3 as averaged over polar angles from 16.5° to 29.0°. Only the LP data have been averaged using mirror symmetry with respect to $[1\bar{1}0]$ direction, which is located at 90° here. The vertical-solid lines show the positions of the forward-focusing peaks observed in the LP data. The dotted lines are estimated peak positions using Eq. (1) with $m=4$.

to the $[1\bar{1}0]$ direction. Because the measurement was done only over approximately the upper half of the pattern, the bottom half was produced simply by rotating the upper half by 180°.

We can see basically six peaks in each of the patterns of Fig. 3. The average azimuthal angles of these peaks as measured relative to the $[001]$ direction are 28°, 90°, and 152°. These angles also correspond reasonably closely with the angles of the forward scattering peaks observed in high-energy x-ray photoelectron diffraction (XPD),[4] which are 25°, 90°, and 155°. The white fiducial lines show the average direction of these peaks as derived from the LP data, and it is clear that there is a tendency for the pattern to shift counter-clockwise with LCP excitation in Fig. 3(b). Such peak ''rotations'' are of the same qualitative type as seen by Daimon *et al.* for Si(001).[1]

In order to discuss these rotations more quantitatively, we have first averaged the data in Fig. 3 over the full polar-angle range studied and the resulting curves are plotted in Fig. 4.

The circles and squares in Fig. 4 are the ϕ dependence of the averaged peak intensities for LCP and LP, respectively, over a polar take-off angle range from 16.5° to 29.0°. As described above, the LP data have been averaged using mirror symmetry with respect to the $[1\bar{1}0]$ direction, which is 90° here.

The vertical-solid lines show the average positions of the peaks (probably dominated by single-forward scattering) determined for the LP case in Fig. 3(a) and we denote these peaks by A_{LP}, C_{LP}, and B_{LP}. The vertical-dotted lines are now estimated from the formula of Daimon *et al.*[1] for such peak-rotation phenomena:

$$\Delta\phi = \frac{m}{kR\,\sin^2\theta},\qquad(1)$$

where $\Delta\phi$ is the azimuthal shift, m is the magnetic-quantum number in the final-state photoelectron wave function, k is

the wave number of the photoelectron, R is the internuclear distance between the emitter and a nearest-neighbor scatterer, and θ is the polar angle between the photon-incident direction and the outgoing photoelectron direction.

The photoelectrons are from the W $4f$ core level, and the outgoing g or $l=4$ channel is expected to be dominant due to its larger radial matrix element. Furthermore, within this g channel, the $m=4$ state should make the strongest contribution to intensity due to angular integrations in the dipole matrix elements.[1] From Eq. (1), it is thus also clear that using $m=4$ will provide an estimate of the maximum azimuthal shift of a given peak.

Using the known structural parameters for this oxygen overlayer,[4] $\Delta\phi$ is calculated to be 15.9° for the A and B peaks and 18.6° for the C peak using the m value of 4, and these values are indicated by the vertical-dashed lines in Fig. 4. For all peaks in the LCP curve, A_{LCP}, C_{LCP}, and B_{LCP}, we see very good agreement as to the prediction of the maximum $\Delta\phi$.

IV. SUMMARY

The diffraction peaks of chemically shifted W $4f$ photoelectrons from atoms bound to oxygen in the W(110)1×1-O structure show a similar peak-rotation pattern to those observed in a previous Si(001) experiment.[1] The maximum rotation angles are in good agreement with those calculated using Eq. (1) with an m value of 4. Hence, the phenomenon of peak rotation with circular polarized excitation seems to be very general, and Eq. (1) represents a reasonable first-order way to describe it. This formula has also been derived recently within a more exact quantum-mechanical scattering theory by Chasse and Rennert.[9]

Such peak-rotation effects with CP excitation are thus expected to occur in both nonmagnetic and magnetic systems, and to be important ingredients of any quantitative description of core photoelectron angular distributions from such systems. Particularly since excitation of spin-orbit-split core levels such as those of W with CP radiation have been shown to exhibit very high degrees of spin polarization,[10] the interplay between spin-dependent scattering effects and these nonmagnetic effects is an important consideration in applications to magnetic materials.

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