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Surface core-level shifts at vicinal tungsten surfaces

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Core-level $4f_{7/2}$ photoemission spectra are measured for W(110) and for two stepped-surface planes along the {100} zone: W(540) and W(320). The vicinal-surface spectra are fit using a four-component Doniach-Sunjic–Gaussian function with variable parameters that allow independent variation in the peak locations and intensities based on the different nearest-neighbor coordination of surface atoms. The new experimental results differ significantly from all prior experimental studies of surface core-level shifts associated with vicinal tungsten surfaces. Surface step-atom core-level binding energies obtained from the photoemission spectra are found to be in excellent agreement with simple local-coordination models and initial-state shifts from *ab initio* calculations of surface core-level shifts and confirm general trends associated with application of coordination models to both low- and high-index tungsten surfaces. No compelling evidence of coordination-dependent final-state effects is observed. Effects on core-level spectra and surface core-level shifts associated with surface hydrogen dose are investigated. Vicinal surface spectra of tungsten are shown to be more sensitive to hydrogen doses than parent low-index surfaces, possibly accounting for prior difficulty in obtaining consistent core-level photoemission spectra for vicinal tungsten surfaces.

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I. INTRODUCTION

Atoms at a crystal surface experience lower coordination than corresponding bulk atoms. The inherent difference between the local structural and electronic environments of bulk and surface atoms are known to produce shifts in core-electron binding energies. Surface atom core-level shifts (SCLS) have been studied by photoelectron spectroscopy for a broad range of low-index metal and semiconductor surfaces, including additional chemical shifts induced by adsorbates added to the clean surface. The SCLS experiments have been supported by an equally broad range of calculations that explore the relationship between local atomic coordination and electronic structure and the core-level binding-energy shifts measured by photoemission. This body of work has resulted in a good understanding of chemical shifts in core-electron binding energies that is now routinely exploited in surface chemical analysis: electron spectroscopy for chemical analysis (ESCA).

Vicinal surfaces provide an opportunity to further test and refine models that attempt to relate local atomic coordination and electronic properties to core-level binding-energy shifts.[1–4] A vicinal surface is produced by cutting a crystal at an angle different from those that yield low-index planes thus producing a stepped surface. The present paper deals with vicinal surfaces derived from a bcc (110) surface by cutting the crystal 6.3° (540) surface, or 11.3° (320) surface from the (110) plane around the [001] crystallographic axis. Figure 1 displays the (unreconstructed) surface atomic geometry of these three surfaces. Several types of atoms can be identified based on the local atomic coordination. While theoretical models[1,4] of SCLS for vicinal tungsten surfaces distinguish terrace atom types by accounting for second- and higher-neighbor coordination, for the purpose of discussions in the present work, only four distinct types of atoms are considered and identified in Fig. 1: step-edge atoms, terrace atoms, corner atoms, and bulk atoms.

These surface models and the assumption of only four distinct types of atoms contributing to core-level photoelectron spectra for the (110)-based vicinal surfaces of tungsten are well justified by prior experiments and calculations. While low-energy-electron diffraction (LEED) studies of bcc (100) surfaces of W (and Mo) have identified intrinsic (clean surface) reconstruction,[5,6] the more densely packed unreconstructed W(110) surface has been shown to be thermodynamically stable. Exposure of the W(110) surface to approximately 2L [1 L (Langmuir)$=10^{-6}$ Torr s] of H_2, corresponding to a surface coverage $\theta \sim 0.5$ monolayer, destroys the symmetry of conjugate LEED beams[7] associated with a mirror plane. The new H-induced symmetry is attributed to a shift in first-layer atoms; a reconstruction that persists at room temperature even though the H overlayer is disordered. However, LEED crystallography[8] of clean W(110) including vicinal surfaces derived from the W(110) surface (to simulate surface roughness) did not manifest any evidence of reconstruction. Also, Purcell *et al.*[2] cited unpublished work by Adams (Ref. 44 of their paper) who found no evidence of lateral reconstruction on W(310). Therefore, all three models of unreconstructed surfaces displayed in Fig. 1 can reasonably be assumed to be valid.

Prior experimental studies of $4f$-shell core-level photoemission from W(110) (Refs. 9–12) have established the properties of the surface core-level spectra. The close-packed W(110) surface is ideal for studying mechanisms that govern line shapes and core-level shifts. The intrinsic photoemission line widths of $4f$ states are narrow (long lifetime of the excited state) and the bcc lattice geometry results in nearest- and next-nearest-neighbor coordination of second-layer atoms identical to the bulk values. These features of atomic coordination and $4f$-shell photoemission from W(110) suggest only four peaks should be observed from the $4f_{5/2}$ and $4f_{7/2}$ states. Distinct lines from several surface layers can be resolved in cases where the local coordination converges more slowly to the bulk value and where a low density of states yields long electron mean-free paths [i.e., SCLS for

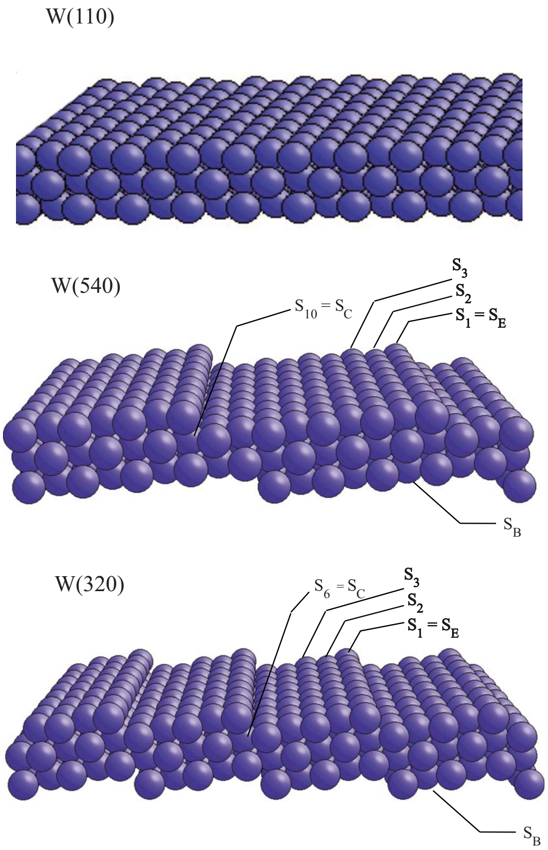

FIG. 1. (Color online) Atomic structure of (unreconstructed) W(110), W(540), and W(320). Rows of surface atoms having different coordination are identified. S_E are step-edge atoms, and S_C are atoms that lie under S_E. Terrace atoms S_T are surface atoms $S_2 - S_9$ for W(540) and $S_2 - S_5$ for W(320). S_B designates bulk atoms.

four layers at Be (0001) have been reported]. Temperature-dependent high-resolution photoemission studies of the $4f_{7/2}$ bulk and surface peaks from W(110) (Ref. 9) have been used to accurately characterize the SCLS of the $4f_{7/2}$ surface peak (321 ± 1 meV shift from the bulk peak value) and the phonon (Gaussian) width of the bulk and surface peaks at 210 K (45.4 and 48.4 meV) and at 310 K (57.3 and 65.6 meV). The singularity index α, associated with screening charge, was also determined for the bulk and surface peaks (0.035 and 0.063). These parameters are used later in the line shape analysis and curve-fitting exercises required to interpret the SCLS of W(540) and W(320).

While several experimental studies of SCLS for vicinal surfaces derived from W(110) have been reported,[1–3] the results and conclusions are inconsistent and are not in very good agreement with corresponding theoretical work.[1,4] The theoretical results for W(320) SCLS are in good agreement: tight-binding[1] and *ab initio*[4] results both predict S_1 atom core-level shifts of 0.34–0.36 eV. Smaller core-level shifts are predicted for surface atoms having higher first neighbor coordination: S_2 atoms 0.18 eV, $S_3 - S_5$ atoms 0.25 eV, and $S_6 = S_c$ atoms 0.06 eV. With reasonable assumptions about the spectral weight (proportional to the number of a specific type of surface atoms) and line shape [component lines that do not depart significantly from the W(110) surface peak shape], the theoretical predictions suggest that the W(320) $4f_{7/2}$ photoelectron spectrum should closely resemble (at the same photon energy) the W(110) spectrum with a slightly smaller SCLS peak shift (from the terrace atoms $S_3 - S_5$), a broader surface peak width (due to contributions from S_1 and S_2); and possibly a resolved shoulder (from S_1) associated with the largest SCLS resulting from the lowest atomic coordination.

Experiments[1–3] carried out on vicinal W(110) surfaces that were intended to test local-coordination models of surface core-level shifts, and more specifically test *ab initio* predictions for $4f_{7/2}$ spectra from W(320), have produced conflicting results. Detailed comparisons can be studied by referring to tables presented in the relevant referenced published work.[2,4] The step-edge atoms (S_1) have the lowest coordination of all atoms on the W(320) surface, and all models predict that these atoms should exhibit the largest core-level shift. A general idea of the experimental inconsistencies for $4f_{7/2}$ core-level shifts on vicinal tungsten surfaces can be obtained by considering the measured values of S_1 atom core-level shifts: Ref. 1, 580 meV; Ref. 2, 410 meV; and Ref. 3, model dependent with values ranging from 270–310 meV. This large range of experimentally determined values for the S_1 $4f_{7/2}$ core-level shift on W(320) suggests systematic errors in the measurements based on the fact that corresponding results for the (single-atom-type) SCLS from the low-index W(110) surface[1–3] are consistent in yielding values in good agreement with the accepted value[9] of 321 meV.

Two of the prior SCLS experiments on W(320) (Refs. 1 and 2) attempted to use the photon-energy dependence of the $4f_{7/2}$ line shape to distinguish between contributions from the various types of surface atoms. Such dependencies can be expected based on electron mean-free-path effects, photoabsorption cross-section effects, and multiple-scattering-diffraction effects. Inconsistencies between the first two SCLS experiments for W(110) $4f$-shell photoemission, specifically, the quoted SCLS's for S_1 (540 and 410 meV), coupled with the significant departure from the theoretical value (340 meV) motivated a third experimental attempt[3] to accurately characterize the $4f_{7/2}$ SCLS for W(320).

The third experiment[3] failed to resolve the inconsistencies in W(320) S_1 $4f_{7/2}$ SCLS, but did address possible origins of experimental inconsistencies and systematic errors in prior experiments. By using a bifacial W(110)/W(320) crystal, it was possible to unambiguously identify the bulk $4f_{7/2}$ peak of the W(320) spectra at all photon energies, which eliminated erroneous assignment of the bulk peak contribution to measured W(320) spectra. In addition, systematic studies of the angle-resolved photon- and emission-angle-dependent line shapes of the bulk and surface peaks of W(110) (Ref. 12) were used to assess the cross-section and scattering dependencies. These systematic experimental studies, in conjunction with extensive curve-fitting exercise for both W(110) and W(320) spectra, resulted in the conclusion that only three of the five terrace rows are electronically equivalent to W(110), i.e., that the S_1 and S_5 rows can be distinguished from other terrace atoms by their SCLS and that the S_1 SCLS was of the order of 310 meV. The more recent results[3] also suggested that some of the peak components in prior experimental studies of W(320) may have been incorrectly assigned.

The present paper presents new $4f_{7/2}$ photoemission spectra from W(110), W(540), and W(320) that appear to resolve the disagreements between prior experiments and between experimental and theoretical results for the W(320) SCLS. The new SCLS results for W(320) are in very good agreement with theoretical predictions, and the additional spectra for W(540) are compatible with expectations based on SCLS models. The effects of H_2 dosing on the SCLS are examined experimentally, and it is found that vicinal-surface $4f$ spectra are significantly more sensitive to contamination by H_2 than the low-index W(110) surface, possibly accounting for some of the prior experimental inconsistencies.

II. EXPERIMENT

The single-crystal W boule was aligned using x-ray Laue techniques, assisted by ORIENT EXPRESS software,[13] and cut using an electric-discharge wire saw. Additional application of Laue techniques during the mechanical polishing stage of surface preparation resulted in alignment accuracy of the (110), (540), and (320) surfaces of $\pm 0.5°$. *In situ* preparation of clean surfaces was accomplished using standard methods: repeated electron-beam heating of the crystal at 1520 K in 10^{-7} Torr oxygen followed by flashing to 2300 K in a vacuum of 1×10^{-10} Torr. Low-energy-electron-diffraction was used to verify the quality of the surface order (including the expected splitting of diffracted beams from the vicinal surfaces). Core-level spectra ($4f_{7/2}$ state) as a function of hydrogen dose (described later) was used to systematically evaluate the effect of low-coverage hydrogen on the SCLS of the low-index W(110) and vicinal W(320) surfaces.

The photoemission studies were carried out using the University of Texas 6 m toroidal-grating monochromator[14] at the CAMD storage ring located in Baton Rouge, Louisiana. A 150 mm hemispherical analyzer equipped with multichannel electron detection was used to measure the spectra. The combination of high monochromator flux resulting from optics that accept 28 mrad of bending-magnet radiation[14] and efficient photoelectron detection permitted spectra with low statistical noise to be obtained in less than 60 s (all prior experiments required several minutes). Our core-level spectra were signal averaged to $\sim 10^4$ counts/channel at the dominant (bulk) peak yielding statistical errors in the spectra of $\sim 1\%$. The electron energy analyzer was operated at a pass energy that produced analyzer resolution of approximately 30 meV. Fermi edge scans were used to evaluate the overall instrument (monochromator+analyzer) energy resolution which was varied from 70–100 meV, and modeled as a Gaussian function. The monochromatized synchrotron radiation was incident on the sample at 45° with polarization parallel to the step edges, and photoelectrons were collected along the surface normal with a collection cone (analyzer acceptance) of about 18°. Some off-normal spectra were measured, also with an 18° acceptance cone. Sample temperature was monitored using a W/Re thermocouple spot welded to the tungsten crystal, and all spectra were measured immediately after the sample temperature had returned to near 300 K after flashing. The absence of oxygen contamination was probed after SCLS spectra had been taken by searching for photoemission from oxygen (O_{2P}). The level of hydrogen contamination was judged by the SCLS of the S_1 shoulder obtained from hydrogen dose studies described later.

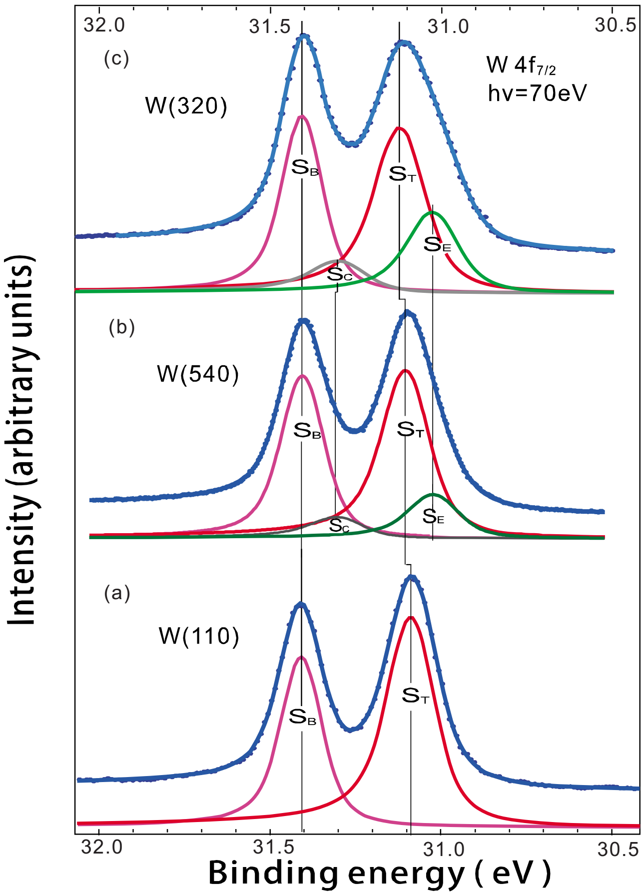

FIG. 2. (Color online) Photoemission spectra for W(320), W(540), and W(110). The W(110) spectra is fit using a two-line function; W(540) and W(320) spectra are fit using a four-line function (refer to text). The component peaks are the bulk peak, S_B; the corner atom peak, S_C; the terrace-atom peak, S_T; and the step-edge peak, S_E.

III. SURFACE CORE-LEVEL SPECTRA

Figure 2 displays surface and bulk peaks produced by $4f_{7/2}$ photoemission from W(320), W(540), and W(110) surfaces. The photon energy used (70 eV) allows direct comparison with a corresponding spectra for W(110) reported by Riffe *et al.*[9] The curve fitting for the W(110) $4f_{7/2}$ spectra was based on the same two-component analysis and parameters reported by Riffe *et al.*:[9] two fully independent Doniach-Sunjic (DS) lines convoluted with independent Gaussian functions that account for the phonon (57.3 meV bulk and 65.6 meV surface) and instrument (70 meV) broadening. Best fits were obtained using the separate bulk and surface lifetime widths and singularity index values obtained by Riffe *et al.*[9] (surface: $w=80$ meV and $\alpha=0.063$; bulk: $w=65$ meV and $\alpha=0.035$) convoluted with the above-quoted Gaussian width for surface and bulk phonon broad-

TABLE I. Comparison of SCLSs for different works (All SCLSs in units of meV). Note that minus sign has been omitted and positive numbers correspond to lower binding energy.

		Surface/terrace (S_T)	Step edge (S_1)	Corner (S_C)
W(110)	This work	318 ± 3		
	Riffe *et al.*	321 ± 1		
	Theory	300		
W(540)	This work	304 ± 7	380 ± 7	108 ± 12
W(320)	This work	280 ± 7	380 ± 7	114 ± 12
	Riffe *et al.*	180–200	270–315	Negative
	Purcell *et al.*	250	410	10
	Chauveau *et al.*	300	580	180
	Theor. (TBA)	250–290	340	18
	Theor. (*ab initio*)	180–250	360	6

ening in quadrature with the 70 meV (Gaussian) instrument resolution function. Analysis of the SCLS for W(110) $4f_{7/2}$ [Fig. 2(a)], yields a shift of 318 ± 3 meV in good agreement with the result obtained by Riffe *et al.*[9] and with the result reported in our prior work on W(110).[3]

A corresponding four-component curve-fitting procedure was used to model the peak structure of the $4f_{7/2}$ W(540) and W(320) spectra. Restricting the curve fitting to four peaks (Fig. 1) is justified based on the results of both TBA[1] and *ab initio*[4] calculations that predict terrace-atoms S_3, S_4, and S_5 all should have very similar SCLS (in the range of 250 ± 40 meV). The curve-fitting procedure was initiated using four peaks (for bulk, S_1, S_T, and S_C) with weights corresponding to the relative number of surface-atom types and the total bulk-to-surface weight equal to the result for W(110), and with SCLS adjusted to the (*ab initio*) calculated values. The peak-shape parameters for the surface (S_1 and S_T) and bulklike (S_C, bulk peaks were fixed at the values just cited that were used to fit the W(110) spectra. The relative peak positions (compared with the bulk) and peak weights (compared with the bulk) were allowed to vary until a best fit of the experimental data was achieved. The model and fitting procedure yielded excellent fits (compare solid lines in Fig. 2 with data points) with a residual distribution (difference between data and fit) described by a Gaussian having width corresponding to the expected statistical error.

The resulting component peaks and the line fits to data are displayed in Fig. 2 and the SCLS shifts are listed in Table I. The quality of the fits and consistency of the SCLS's for W(320) and W(540) provide strong evidence of the validity of the model and parameters. Error bars assigned to the major peaks in Table I (S_T and S_1) are based on the quality of the fit as the binding-energy parameters are varied. The values ± 3 meV are compatible with prior results quoted by Riffe *et al.*[9] for W(110) SCLS of 321 ± 1 meV who also signal averaged peak intensity to $\sim 10^4$ counts/channel. The four-peak model adds two more degrees of freedom, and reduces peak location certainty. As a check on the accuracy of the fitting procedure, we note that the S_c peak for W(320) and W(540) should have essentially the same binding energy based on identical local coordination. The experimental values obtained from the fitting (Table I) are very close: 108 ± 12 meV for W(540) and 114 ± 12 meV for W(320).

The tabulated experimental and theoretical (*ab initio*) SCLSs have slightly different meaning. The experimental values are obtained from excitation spectra and reflect both initial-state and final-state effects. Initial-state SCLSs are defined by the difference between eigenvalues of a specified core level at different surface-atom locations. The initial-state effect is a ground-state property that is related to the self-consistent potential and local charge density. The final-state SCLS takes account of core-hole screening that occurs when the photoelectron leaves the crystal and is calculated from the total-energy difference between crystals containing a core hole at different atomic positions. The screening process can produce line shape asymmetry which can be seen as a tail in the high binding energy half of the peak components (in Fig. 2), as well as shifts in the SCLS. The *ab initio* calculations predict final-state SCLS's for W(320) of $\Delta S_1 = 0.13$ eV, $\Delta S_2 = 0.06$ eV, $\Delta S_3 = \Delta S_4 = \Delta S_5 = 0.07$ eV, and $\Delta S_6 = 0.04$ eV. An interesting feature of the *ab initio* calculations for W(110) is the prediction of a small negative final-state SCLS $\Delta S_5 = -0.05$ eV. The sign difference between the final-state SCLS $\Delta S_5 = -0.05$ eV for W(110) and $\Delta S_1 = +0.13$ eV for W(320) results in interesting consequences when compared with the corresponding experimental results. Including the final-state shift brings the *ab initio* result for the SCLS of W(110) into better agreement with the experimental value: $\Delta S_{\mathrm{theor}} = -0.30$ eV, $\Delta S_{\mathrm{expt}} = -0.321$ eV. The opposite result occurs for W(320) where better agreement with the experimental value for $\Delta S_1 = -0.380$ eV is obtained by neglecting the (positive) final-state SCLS: $\Delta S_1 = -0.36 + 0.13 = -0.23$ eV compared with the experimental value $\Delta S_1 = -0.38$ eV. Clearly, there remain discrepancies between the experimental and theoretical picture of SCLS associated with W(110) and W(320) SCLSs. However, as will be demonstrated in Sec. IV, the general picture of SCLS behavior is significantly improved by the new experimental results.

IV. EFFECT OF HYDROGEN DOSES

Prior experiments have studied the effect of alkali-metal[10] and hydrogen[11] adsorption on the surface-atom $4f$ core-level shifts of W(110). In the case of hydrogen adsorption, two

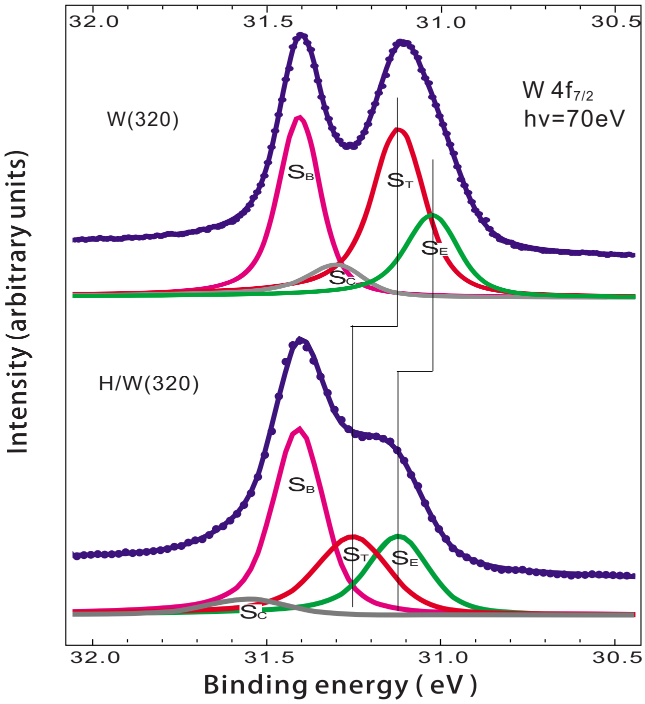

FIG. 3. (Color online) Photoemission spectra for clean and H-dosed W(320). The H-dosed spectra is decomposed to the four lines that fit the data: S_B, S_T, S_C, and S_E.

distinct effects were observed: a chemical shift at low coverage ($\theta < 0.5$ ML) that scaled according to 120 meV/ML [1 ML$=p(1\times1)$ coverage] and a larger shift (250 meV/ML) from the (previously mentioned) H-induced surface reconstruction[7] that occurs for $0.5 < \theta < 1.0$ ML (total SCLS ~225 meV at $\theta = 1$). LEED studies of multilayer relaxation at W(110) (Refs. 8 and 15) have established the sensitivity of surface atomic geometry (top-and-second-layer relaxation) to H coverage ($\theta < 0.5$ ML). The LEED experiments as well as the compatible data from 4*f* core-level experiments, show that clean surfaces of W(110) can be prepared and maintained long enough to obtain experimental results corresponding to an intrinsic (clean) surface.

Our prior photoemission experiments[3] on W(110) and W(320) used a bifacial crystal to eliminate any questions regarding correct assignment of the bulk peak when photon energies and emission angles were varied: Fig. 2 in (our prior work) Ref. 3 displays data set pairs for W(110) and W(320) taken using the same (bifacial) sample at several different photon energies (60 and 90 eV) and using different emission angles. While the W(110) surface spectra in our prior experiment are in good agreement with other published "clean" surface $4f_{7/2}$ spectra[9–12] [and with Fig. 2(a)], our prior W(320) spectra, which were taken using the same (bifacial) sample and under identical preparation and measurement conditions, appears to be similar to the spectra for W(110) after exposure to 2–3 L of H_2 (Fig. 3) and Ref. 11. This low dose of H_2 is known to result in approximately 0.5 ML of H on W(110). In view of the new $4f_{7/2}$ spectra for W(110), W(540), and W(320) shown in Fig. 2, which we now judge to represent clean surface results, the conclusion is that vicinal surfaces of tungsten, specifically W(320) are significantly more susceptible to H contamination from residual gas than the flat W(110) surface. Data acquisition times for Fig. 2 spectra were approximately ten times shorter than for all prior experiments due to the availability of higher photon flux at the required energy resolution and multichannel electron deflection.

The experiments carried out in the present study support the conclusion that stepped W(110)-based surfaces exhibit more rapid H uptake than (flat) W(110) surfaces. Qualitatively, it was found more difficult to obtain and maintain the clean surface spectra shown in Fig. 2 for W(540) and W(320) than for W(110). A more quantitative picture of the H-induced degradation of the 4*f* spectra from W(320) is shown in Fig. 3 in which a clean W(320) spectra are compared with the corresponding spectrum obtained after a low (~1 L) does of H [that has been shown to produce an H coverage on W(110) of $\theta < 0.5$ ML]. The resulting W(320) +H spectra can be compared with the W(110)+8.6 LH reported by Riffe *et al.*[11] [which is essentially the same as our own results for H saturation coverage on W(110)]. These $4f_{7/2}$ spectra demonstrate the sensitivity of W(320) to residual H_2 and help explain the substantial problems encountered in obtaining valid $4f_{7/2}$ core-level spectra for vicinal tungsten surface in prior studies.[1–3] Enhanced chemical activity (dissociative chemisorptions of H_2 in particular) is commonly observed on stepped surfaces suggesting that the corner atom sites or step-edge sites are more chemically active in promoting dissociation. Comparison of the results of curve fitting the clean (Fig. 2) and H-dosed (Fig. 3) W(320) spectra reveal that both the S_E (edge atom) peak and the S_2–S_4 (terrace atom) peak contributions to the H-dosed spectra are shifted back toward the bulk peak (terrace-atom peak approximately 120 meV and edge-atom peak approximately 100 meV). The terrace-atom chemical shift is consistent with prior results quoted by Riffe *et al.*[11] who reported a hydrogen-induced chemical shift of the $4f_{7/2}$ SCLS for W(110) of 120 meV at low H coverage.

V. DISCUSSION

Prior studies of W $4f_{7/2}$ SCLS carried out using low-index surfaces [W(100), W(111), and W(110)] as well as several vicinal surfaces have established the importance of atomic coordination in determining the core-level binding energies of surface atoms. A simple coordination model that weights contributions to displaced local charge density by the coordination number normalized to radial distance (based on Smoluchowski smoothing effect[16]) seems to account for the observed trends in SCLS of the low-index W surfaces. Close-packed bcc surfaces maximize the difference between the coordination of step-edge and terrace atoms, and the previously mentioned experiments have attempted to explore the coordination model of SCLS based on measurement of the edge atom SCLS. A troubling feature of prior vicinal surface SCLS experiments are the previously noted discrepancies between the various experiments and between several theoretical results (which are internally consistent) and the experiments, specifically for the edge atom (S_1) SCLS (Table I).

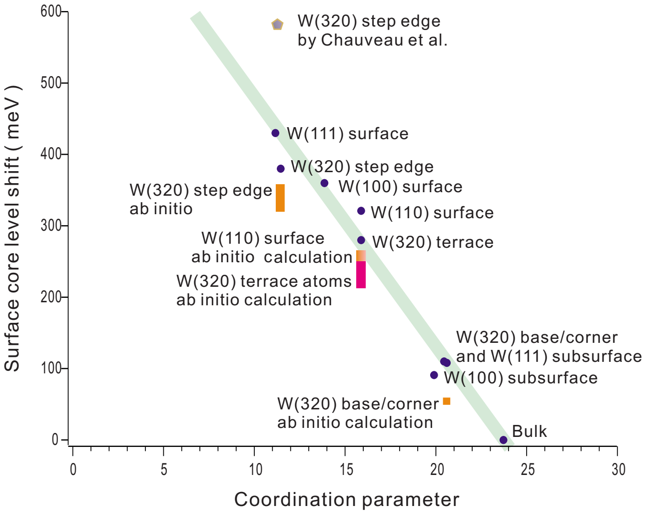

FIG. 4. (Color online) Plot of the SCLS for various tungsten surface atoms on both low- and high-index surfaces, as a function of the coordination parameters C [Eq. (1)]. All experimental points (solid circles) (except the result for W(320) S_1 by Chauveau *et al.* (solid pentagon) are believed to be valid (refer to the text). The bars for *ab initio* calculations represent the range of values including initial-state effects.

Our new results, quoted in Table I, resolve the discrepancies. Figure 4 displays a plot of W $4f_{7/2}$ SCLS (relative to the bulk binding energy) for the low-index W surfaces and for two vicinal surfaces [W(520) and W(320)] as a function of the coordination parameter,

$$C = \sum_{j=1}^{3} n_j/r_j. \tag{1}$$

In Eq. (1), n_j is the atomic coordination number of a specific surface-atom type, r_j is the distance to first nearest neighbor (nn) ($j=1$), second-nearest neighbor (nnn) ($j=2$), and third nearest neighbor (nnnn) ($j=3$). Values of r_j and nearest-neighbor coordination numbers for the various types of surface atoms are shown in Table II. For clarity of presentation the only experimental results for vicinal W surfaces that are plotted are our new results for W(540) and W(320) and the prior value for the S_1 (step-edge) atom of W(320) reported by Chauveau *et al.*[17] (540 meV) which serves to illustrate the existing discrepancy. Also only the initial-state SCLS for W(110) and W(320) step edge and terrace atoms obtained from the *ab initio* calculation are displayed in the Fig. 4.

The impressive correlation between $4f_{7/2}$ SCLS for atoms at W surfaces [now including W(540) and W(320) stepped surfaces] and coordination parameter C illustrated by Fig. 4 suggests that the simple coordination model essentially accounts for SCLS. The data presented are selected, and it is important to address the criteria used for selecting or rejecting specific prior results for presentation in the figure. The SCLS data for high-symmetry surfaces W(100), W(111), and W(110) are judged to be accurate. Early SCLS for W(100) and W(111) reported by Van der Veen *et al.*[18] were reproduced by Wertheim *et al.*[19] to an accuracy of ±10 meV, and the quality of the spectra and fits appear to be very good. Similar comments apply to SCLS data for W(110) reported by Riffe *et al.*[9] which are consistent with our prior[3] and new results. Minor differences in (Doniach-Sunjic) line shape parameters were used in fitting the W(100) and W(111) SCLS spectra, but the magnitude of SCLS and relative amplitudes of surface components have been shown to be insensitive to the variation in these parameters.[19] Based on these features of SCLS for the low-index W surfaces, the data presented for W(100), W(111), and W(110) are judged to be highly accurate.

Only one SCLS from prior studies[1–3] of vicinal W surfaces is presented in Fig. 3. The large shift (580 meV) for the $4f_{7/2}$ SCLS of step-edge atoms on W(320) reported by Chauveau *et al.*[1] is very likely due to systematic errors in binding-energy calibrations and incorrect peak assignment. The large discrepancy between the result of Chauveau *et al.*[1] and the corresponding result of Purcell *et al.*[2] was discussed by Riffe *et al.*[3] and by Purcell *et al.*[2] The basis for the sys-

TABLE II. Coordination numbers and surface core-level shifts for several different tungsten surfaces. n_1 defines the number of nearest neighbors, n_2 defines the number of second-nearest neighbors, and n_3 defines the number of third nearest neighbors.

Tungsten surface	SCLS (meV)	n_1	n_2	n_3	C
W(100) surface	360	4	5	6	13.86
W(100) subsurface	91	8	5	8	19.90
W(111) surface	430	4	3	5	11.16
W(111) subsurface	110	7	6	9	20.45
W(110) surface	321	6	4	7	15.88
W(320) step edge	380	4	4	4	11.45
W(320) terrace[a]	280	6	4	7	15.88
W(320) base/corner[b]	108	8	5	9	20.60
W(540) terrace[a]	280	6	4	7	15.88
Bulk	reference	8	6	12	23.72

[a] Atom 2 has six third nearest neighbors.

[b] Base atom has six nearest neighbors.

tematic error claim can be seen by comparing the (normal emission) 52 and 65 eV spectra in Fig. 5a of Chauveau *et al.*[1] with corresponding results presented in Fig. 2 of Kim *et al.*[12] Chauveau *et al.* modeled their [W(320)] spectra with no bulk contribution; yet Fig. 2 of Kim *et al.*[12] clearly showed [for W(110)] that the photon-energy dependence of the bulk-to-surface peak is only weakly modulated as photon energy is swept from 64 to 120 eV. The 580 meV SCLS can reasonably be attributed to monochromator calibration errors and incorrect peak assignment. Plotting the 580 meV (only experimental value judged to be unreliable in Fig. 3) does serve to illustrate the large discrepancy between theoretical prediction and prior experiments for the SCLS of W(320) step-edge atoms.

Two other results from prior SCLS studies of W(320) listed in Table I are not plotted in Fig. 3 because they are judged to be unreliable. Comparison of the 70 eV W(110) $4f_{7/2}$ spectra of Fig. 2 (this paper) with corresponding results reported by Purcell *et al.*[2] (Fig. 5), Riffe *et al.*[3] (Fig. 2, 60 eV), and Chauveau *et al.*[1] (Fig. 4) that also reported W(320) spectra shows that all prior experiments on stepped W surfaces obtained compatible results for W(110). There are clearly observable variations in the achieved energy resolution and statistical precision (compare spectra in Refs. 1–3 with Ref. 9–11 and with Fig. 2). But the SCLSs from all of these spectra are similar and near the accepted value of 321 meV which is plotted in Fig. 3. This compatibility of results does not persist when comparing W(320) spectra. For example, the 70 eV spectra of clean W(320), Purcell *et al.*[2] (Figs. 4 and 5), and Riffe *et al.*[3] [Figs. 2a and 2b (at 60 eV)] resemble the H-dosed spectra shown in Fig. 3. Also note that the W(320) spectra (Fig. 5 of Purcell *et al.*[2]) are shown with a significant shift of what must be the bulk peak relative to the bulk W(110) spectra, and all of the spectra shown in the paper of Purcell *et al.*[2] exhibit fairly large statistical noise. For these reasons, none of the prior SCLS for W(320) are plotted in Fig. 4 (except for the result of Chauveau *et al.*[1] which serves to represent prior systematic errors).

VI. CONCLUSIONS

Analysis of new $4f_{7/2}$ photoemission spectra for W(320) and W(540) vicinal surfaces yields coordination-dependent surface core-level shifts that are in good agreement with simple coordination models and with *ab initio* calculations. The new results differ significantly from prior experimental results, but systematic experiments in which SCLS from (vicinal) W(320) are studied as a function of H_2 dose suggest that additional H-induced chemical shifts and uncertainties in peak assignments at different photon energies account for the prior experimental discrepancies. These results bring SCLS for vicinal W surfaces into compatibility with corresponding experimental results for low-index SCLS results, and with the theoretical understanding of SCLSs based on both simple coordination models and more sophisticated *ab initio* calculations.

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