Core-level shifts of low coordination atoms at the W(320) stepped surface

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We study the surface core-level shifts (SCLS's) at the W(320) surface by *ab initio* calculations, including both initial-state and final-state effects. This stepped surface features (110) terraces with five atom rows, separated by single atomic steps. We find that the final-state effect is important for the proper prediction of the SCLS at the W(320) surface. Unlike the W(110) surface where the final-state effect increases the SCLS to lower binding energy, the reverse is true in the W(320) surface, indicating inefficient core-hole screening at the stepped surface. Our results provide a theoretical basis for the interpretation of core-level photoemission spectra from the W(320) surface.

Stepped surfaces have been extensively investigated in the past years for various physical phenomena such as epitaxial growth, chemical reactivity, corrosion, and catalysis.[1–3] Creation of a stepped surface significantly alters the local electronic distribution around the steps. According to the concept of charge smoothing proposed by Smoluchowski,[4] electrons move from the step edge toward the lower terrace in order to lower the kinetic energy of the electrons. The atoms near steps undergo structural relaxations, due to the new forces generated by the redistribution of the electrons. These modifications of the electronic and structural properties at the stepped surface are expected to affect the core-level binding energy of the atoms near steps, influenced by the change in local valence charge density via the Coulombic interaction between the core and valence electrons.[5]

There are few core-level photoemission studies for stepped surfaces. In the cases of the Ir (Ref. 6) and Pt (Ref. 7) stepped surfaces, the analysis of core-level $4f_{7/2}$ photoemission spectra is extremely difficult, because the intrinsic widths of the Ir and Pt core-level peaks are larger than their respective shifts. On the other hand, core-level photoemission study of the W(320) stepped surface[8–10] can be relatively tractable because of its much narrower $4f_{7/2}$ linewidth, comparable to the magnitude of the surface core-level shift (SCLS's).

The W(320) surface is obtained by cutting the crystal at an angle of 11.3° from the (110) plane around the [001] direction (see Fig. 1). In earlier core-level photoemission studies of W(320),[8,9] core-level spectra were well fit by assigning a discrete SCLS to each inequivalent atom composing the (110) terrace, with the largest SCLS (-0.58 eV in Ref. 8 and -0.41 eV in Ref. 9) being assigned to the step-edge atom. This interpretation is consistent with tight-binding calculations[8] or atomic-coordination models[9] where the step-edge atom, which has the fewest nearest neighbors, produces the largest SCLS. However, a recent core-level photoemission study by Riffe *et al.*[10] found that the surface peaks in the W(320) spectra become closer to the bulk binding energy compared with the case of the W(110) spectra, leading to a filling of the valley between the bulk and surface peaks observed in the latter spectrum. From nonlinear least-squares analysis with a variety of model functions Riffe

et al.[10] found that the average SCLS for W(320) is only ~ -0.14 eV, indicating the absence of a large SCLS for the step-edge atom. Thus the determination of the SCLS for the step-edge atom remains controversial, and the interpretation of core-level photoemission spectra from the W(320) surface is still lacking as well.

In this paper we present the results of *ab initio* calculations of the W $4f_{7/2}$ SCLS at the W(320) surface. We find that the electronic density in (110) terrace of W(320) is nearly identical to that on the W(110) surface, except near the step edge. This isoelectronic property for both surfaces results in similar initial-state SCLS's. On the other hand, final-state effects of core-hole screening for the W(320) and W(110) surfaces differ from each other. Unlike in W(110), core holes in (110) terrace of W(320) are found to be less screened than those in bulk atoms, leading to a decrease of the SCLS. Therefore final-state theory explains well recent photoemission spectra[10] in which the surface spectral weight shifts to the bulk binding energy. However, both initial-state and final-state theory calculations predict the largest SCLS for the step-edge atom.

In our total-energy calculations we employ the plane-wave-basis pseudopotential method within the local-density approximation.[11] Norm-conserving spin-orbit averaged relativistic pseudopotentials are generated by the scheme of Troullier and Martins[12] in the separable form of Kleinman and Bylander.[13] Valence spin-orbit splittings are expected to have a negligible effect on core energy levels. We use the Ceperley-Alder exchange-correlation functional,[14] as parametrized by Perdew and Zunger.[15] A plane-wave basis with a kinetic energy cutoff of 30 Ry is used and the **k**-space integration is carried out with 48 points in the Brillouin zone. The surface is modeled by a periodic slab geometry consisting of 41 atomic layers and a vacuum spacing of about 11 Å. A 51-layer slab calculation is found to change the surface relaxations by less than 1%, yielding negligible changes of the calculated SCLS's.

The atoms were allowed to relax along the y and z directions in Fig. 1 until the forces on them were less than 2 mRy/bohr. In Table I we list their interlayer spacings relative to the bulk (320) interplanar spacing, $d_0 = a_0/2\sqrt{13}$, where $a_0 = 3.18$ Å). We find that the interlayer spacings contract down to the fifth one by $\Delta d_{12} = -22.3\%$, $\Delta d_{23} = -0.3\%$,
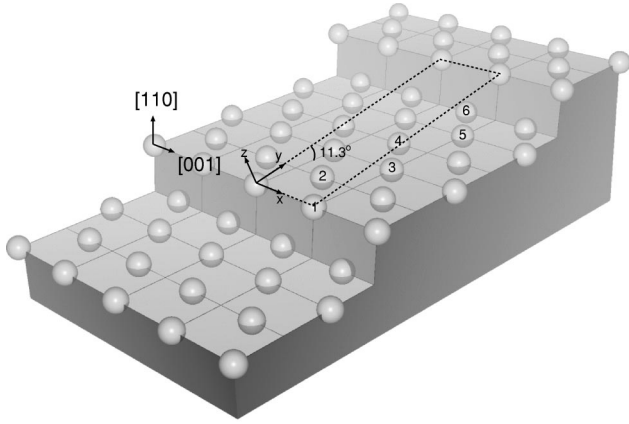
FIG. 1. Atomic structure of the W(320) stepped surface. The dotted line represents the unit cell in the x-y plane.

$\Delta d_{34} = -4.9\%$, $\Delta d_{45} = -15.9\%$, $\Delta d_{56} = -7.0\%$, but the sixth interlayer spacing expands by $\Delta d_{67} = +15.2\%$. To our knowledge, there are no experimental or theoretical data of the interlayer relaxations for this stepped surface, but our results are in accord with the general trend found in the Al and Cu stepped surfaces, in which most of the interlayer spacings between atoms in the terrace exhibit contractions, whereas the interlayer spacing between atoms just below the step edge exhibits expansion.[16–19] The expansion of the sixth interlayer spacing at W(320) can be explained by Smoluchowski[4] smoothing of the electron density. The calculated electronic densities in the yz plane (Fig. 2) show the increased density above atom 6 [the region denoted by the arrow in Fig. 2(b)]. This charge redistribution near the step edge causes atom 6 to relax upward, leading to the expansion of the sixth interlayer spacing. It is interesting to note that the electron densities around atoms 3, 4, and 5 of W(320) are nearly identical to that around the top-layer atom of W(110), indicating that the terrace of the (320) stepped surface has a local environment similar to the (110) surface. For the interlayer relaxations of the W(110) surface our results agree well with those of previous theoretical calculations[20,21] and a recent low-energy electron-diffraction analysis[22] (see Table I).

The initial-state SCLS is defined by the difference of the eigenvalues of a given core level at different sites. Here this shift is calculated from the difference between the expectation values of the self-consistent potential on the bulk and surface W $4f$ atomic orbitals.[23] Our results for the initial-state SCLS are given in Table II. The surface component S_1 for the step-edge atom shifts by -0.36 eV relative to the bulk core level, leading to the largest SCLS to lower binding energy. The shifts for atoms 3, 4, and 5 ($S_3 = -0.23$ eV, $S_4 = -0.23$ eV, and $S_5 = -0.25$ eV) are close to the SCLS (-0.25 eV) for the top-layer atom of W(110). This similar behavior in the initial-state SCLS for both surfaces results from the similar electronic densities between the terrace of the (320) surface and the (110) surface, as mentioned above. On the other hand, the electron density around atom 2 slightly spills out compared with those of atoms 3, 4, and 5, as a consequence of charge smoothing (see Fig. 2). As a result, the shift for atom 2 ($S_2 = -0.18$ eV) is relatively smaller than other surface components. Our initial-state SCLS's are in acceptable agreement with those of the tight-binding calculation,[8] except the prediction of S_6 originating from atom 6 (see Table II): Our result of $S_6 = -0.06$ eV is much smaller than the tight-binding calculation result of -0.18 eV. Note that the tight-binding calculation was carried out using the bulk-truncated W(320) surface. However, the comparison of the initial-state SCLS between the bulk-truncated and relaxed surfaces shows that the SCLS's are changed upon lattice relaxation by less than 0.04 eV (see Table II), implying that small charge redistribution occurs due to relaxation.

The final-state SCLS, taking into account the effect of core-hole screening, is calculated from the total-energy difference of crystals containing a core hole at different atomic positions.[24] We found a change of less than 0.01 eV in the final-state SCLS of W(110) on going from a centered retangular unit cell to a $p(2 \times 2)$. Thus by doubling the W(320) unit cell along the [001] direction we make the interaction between the self-consistently screened core holes sufficiently weak. Our results for the final-state SCLS are given in Table II. The final-state effect due to the screening of the core hole is reflected by the difference between the initial-state and final-state SCLS, given by $\Delta S_1 = 0.13$ 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. Therefore the final-state effect on the step-edge atom is more signifi-

TABLE I. Calculated interlayer relaxations of the W(320) surface. The values are given by the change of the interlayer spacing (%) relative to the bulk interlayer spacing. Here, the negative (positive) sign indicates a contraction (expansion) of the interlayer spacing relative to the bulk one. The results for the W(110) surface are also given, together with previous theoretical and experimental data.

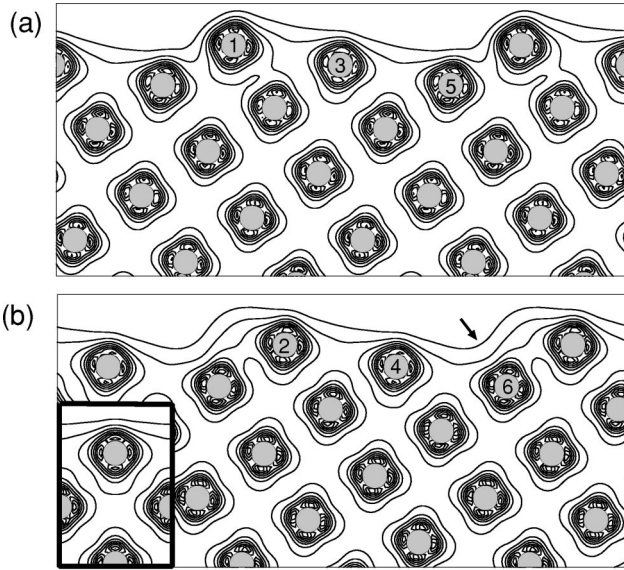|		Δd_{12}	Δd_{23}	Δd_{34}	Δd_{45}	Δd_{56}	Δd_{67}	Δd_{78}	Δd_{89}
W(320)	this	-22.3	-0.3	-4.9	-15.9	-7.0	$+15.2$	-8.0	-0.8
W(110)	pseudopotential[a]	-3.6	$+0.2$						
	FLAPW[b]	-4.1	-0.4						
	this	-3.8	$+0.9$						
	experiment[c]	-3.0 ± 1.3	$+0.2 \pm 1.3$						

[a]Reference 20.
[b]Reference 21.
[c]Reference 22.

FIG. 2. Contour plots of the charge density for the W(320) surface. The plots are drawn in two vertical planes containing atoms (a) 1-3-5 and (b) 2-4-6 (for atom numbers, see Fig. 1). The atomic positions are indicated by filled circles. Contour spacings are 0.8098 $e/\text{Å}^3$. The charge density for the W(110) surface is also plotted in the inset of (b).

cant than on the underlayer atoms. On the other hand, for W(110) the final-state effect has a reverse sign as $\Delta S_1 = -0.05$ eV (see Table II), where the initial-state and final-state SCLS's for the top-layer atom are -0.25 and -0.30 eV, respectively. It is remarkable that final-state effects show disparate features between the W(320) and W(110) surfaces, demonstrating that geometrical roughness influences the sign of the final-state screening contribution. In other words, a core hole on the W(320) stepped surface is less screened than one in a bulk atom whereas the screening of a core hole is enhanced on the W(110) flat surface.

It appears to us that Chaveau *et al.*[8] have misidentified the bulk contribution to their spectra. We note that their bulk peak grows by a factor of about 16 on changing their photon energy from 85 to 95 eV which seems highly unlikely. Riffe *et al.*[10] believe that the spectra of Ref. 8 should be shifted by 0.3 eV to higher binding energy. However, if one believes that the largest contributions to the spectra come from the bulk, the shifts would be smaller for their higher photon energies. In any event, if they have misidentified their bulk contribution, their shifts relative to the bulk would all be meaningless and we choose not to compare our results with their interpretation of their data. Riffe *et al.* also believe that the data of Ref. 9 should be shifted by 0.11 eV to make their W(320) and W(110) core energies identical. This discrepancy could be an experimental artifact or it could arise from different (320) and (110) work functions. Whatever the case, a shift of their spectra will have no effect on their SCLS's which are listed in Table II for comparison with our calculated results. We note that their SCLS's are all negative and larger than our final-state results. Riffe *et al.* were able to fit their spectra equally well in several ways using different numbers of SCLS's, demonstrating that one should use caution in identifying fitting parameters as actual SCLS's. One fit had SCLS's of -0.315, -0.18, and 0.14 eV whereas another had -0.27 and -0.08 eV. Nevertheless, after examining all the experimental data it seems most likely that the screening in our final-state theory is overestimated by the use of static screening, where the core hole is assumed to be completely screened by the addition of an extra valence electron in our slab calculations, maintaining charge neutrality. However, we note that for W(110), where the interpretation of the experimental data is much more straightfoward and consistent,[9,10,25] our final-state SCLS is in perfect agreement with experiment.

In Ref. 10 Riffe *et al.* prepared each sample with both flat and stepped surfaces. They showed four different pairs of curves obtained with different photon energies and scattering geometries. There is considerable difference amongst the W(001) curves but very little amongst the W(320) curves. In Fig. 3 we fit the spectrum from their Fig. 2(d) with the five surface components of S_1 through S_5, S_6 being sufficiently

TABLE II. Calculated initial-state and final-state SCLS (eV) at the the W(320) surface, in comparison with previous initial-state theory. The initial-state results for the bulk-truncated W(320) surface are given in parentheses. Here, the negative sign indicates a lower binding-energy shift. The results for the W(110) surface are also given for comparison.

		S_1	S_2	S_3	S_4	S_5	S_6
W(320)	initial	-0.36	-0.18	-0.23	-0.23	-0.25	-0.06
		(-0.32)	(-0.16)	(-0.21)	(-0.21)	(-0.23)	(-0.05)
	initial [a]	-0.34	-0.25	-0.25	-0.25	-0.29	-0.18
	final	-0.23	-0.12	-0.16	-0.16	-0.18	-0.02
	experiment [a]	-0.41	-0.25	-0.25	-0.25	-0.25	-0.10
W(110)	initial	-0.25					
	final	-0.30					
	experiment	-0.30 [a], -0.31 [b], -0.32 [c]					

[a]Reference 9.
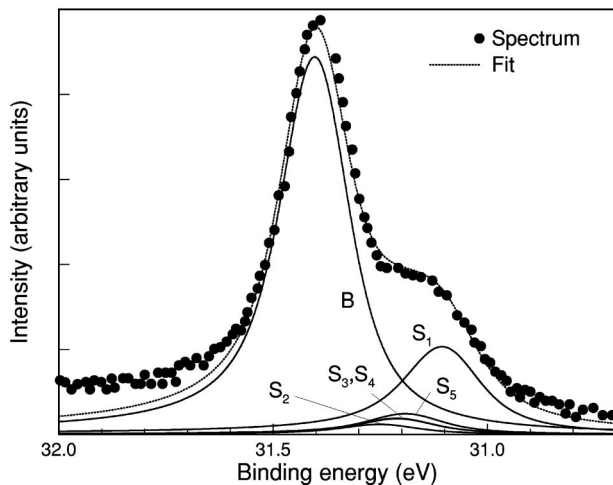[b]Reference 10.
[c]Reference 25.

FIG. 3. Analysis of the W $4f_{7/2}$ photoemission spectrum of the W(320) surface. The data in Ref. 10 are fitted with one bulk line and five surface lines whose peaks are located at $S_1 = -0.30$, $S_2 = -0.15$, $S_3 = -0.19$, $S_4 = -0.19$, and $S_5 = -0.21$ eV, relative to the bulk binding energy (31.6 eV).

close to zero to be ignored.[26] Here we use Doniach-Sunjic[27] lines convoluted with a Gaussian. The fitting parameters are similar to those of the earlier study (Ref. 10): the Lorentzian width and the singularity index for the bulk (surface) component are 68 (80) meV and 0.035 (0.063) except for the Gaussian width of 97 meV for both components. It is surprising that the contribution of the step-edge atom S_1 is so much larger than those of S_2, S_3, S_4, and S_5 but this is consistent with the fit in Ref. 10 where the contribution of the -0.18-eV SCLS which presumably represents the total contribution from atoms 2, 3, 4, and 5 is less than that of the -0.315-eV SCLS from atom 1. We do not understand why the S_1 contribution is so large, but the effects of photoelectron diffraction could play a role in it. Our poor fit of the high binding-energy tail of the experimental curve indicates either that we need one of the SCLS's to be positive, which we doubt is the case, or that the subtraction of secondary electron contributions from the raw data of Ref. 10 was not complete.

In conclusion, we have demonstrated that the final-state effect is essential for the proper prediction of the SCLS at the W(320) surface. Especially, the final-state screening contributions in the W(320) and W(110) surfaces have opposite signs, implying the importance of geometrical effects in core-hole screening. Further, the comparison of our results with experiments provides information that our final-state theory calculations may overestimate screening of the core hole on the W(320) stepped surface, but are successful on the W(110) flat surface. Several features found in the present initial-state and final-state results are anticipated to be prevalent in other metal stepped surfaces.

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