Structure-Dependent $4f$—Core-Level Binding Energies for Surface Atoms on Ir(111), Ir(100)-(5 × 1), and Metastable Ir(100)-(1 × 1)

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Shifts in the core-level binding energies of surface atoms relative to bulk atoms which show a dramatic dependency on surface crystallography have been observed. Surface-atom core-level emission intensities are shown to give direct information on the number of surface atoms, while binding energies give information on the surface-atom coordination number. These data show that the reconstructed Ir(100)-(5×1) face is described by a compressed hexagonal monolayer.

Recent photoemission experiments have reported differences between core-level binding energies for surface and bulk atoms on Au (Ref. 1) and W (Ref. 2). Citrin, Wertheim, and Baer[1] observed a weak asymmetry at the low-binding-energy side of the bulk $4f$ level of polycrystalline Au while Duc *et al.*[2] found the $4f$ surface core-level binding energy of W(110) to be reduced by 0.3 eV relative to the bulk. In this paper we report $4f$–core-level binding energies for surface atoms of Ir(100)-(1×1), Ir(100)-(5×1), and Ir(111) and show for the first time that both emission intensity ratios give direct information on surface structure.

The observed surface core-level shifts reflect initial-state changes in the electrostatic potential in the atomic core region which can be decomposed into configuration changes (rehybridization, etc.) and chemical shifts as well as possible final-state relaxation shifts.[3] The sign of the shift for Ir is towards lower binding energies, as for Au and W(110). However, this is not a general trend as suggested,[2] since our preliminary measurements on polycrystalline Ta show a shift of 0.3 eV towards higher binding energy. The magnitude of the shift for Ir is found to be particularly large (0.68 eV) for the metastable Ir(100)-(1×1) surface and smaller for Ir(100)-(5×1) and Ir(111) (0.49 and 0.50 eV, respectively). Both the shift and surface-to-bulk emission intensity ratio for the Ir(100)-(5×1) surface show that this surface is described by a hexagonal overlayer.

The data were taken with a two-dimensional display spectrometer[4] at the Synchrotron Radiation Center of the University of Wisconsin. Angle-integrated photoelectron spectra were recorded at a photon energy of 100 eV (s-polarized light), yielding a kinetic energy of ~ 40 eV for Ir $4f$ photoelectrons. Since the electron escape depth is very small at this energy (~ 5 Å), the core-level spectra contain an appreciable contribution from the outermost surface layer. The overall system resolution (photons and electrons) was 0.3 eV in this experiment; count rates for the bulk $4f_{7/2}$ peak were typically 5×10^3/sec. Clean Ir(100)-(5×1) and Ir(111) surfaces were prepared by sputter cleaning and repeated cycles of heating in oxygen at 1300 °K and flashing in vacuo to 1500 °K. The clean metastable Ir(100)-(1×1) structure was prepared by following the prescription given in Ref. 5. Surfaces were characterized *in situ* by low-energy electron diffraction (LEED), photoelectron spectroscopy, and Auger-electron spectroscopy {which showed only a small carbon contamination [C(272 eV)/Ir(171 eV) $\lesssim$ 0.03] comparable to that previously reported in Ref. 5}.

An energy distribution curve for Ir(100)-(1×1) is shown in Fig. 1(a). Extra surface-atom peaks are observed on the low-binding-energy (high-kinetic-energy) side of the bulk $4f_{5/2}$ and $4f_{7/2}$ levels. The binding-energy shift of the surface-atom peaks is sensitively dependent on H_2-gas adsorption, as is shown in Fig. 1(b), whereas the binding energy of the bulk peak is unaltered. Upon mild heating, the adsorbed hydrogen was removed and the clean Ir(100)-(1×1) spectrum was regained. Further heating to ~ 800 °K for a few seconds causes a conversion to the (5×1) structure. The corresponding surface core-level shift, as shown in Fig. 1(c), is significantly less than for the (1×1) structure. This agrees with the intuitive notion that the equilibrium (5×1) phase corresponds with a more "bulklike" arrangement of surface atoms than the metastable (1×1) phase.

The $4f_{7/2}$ line shapes have been decomposed into bulk and surface contributions as follows. First, a linear background of secondary electrons was subtracted from the original spectra. Bulk and surface components, including the low-binding-energy tails from the bulk and surface $4f_{5/2}$ level, were each represented by theoretical Doniach-

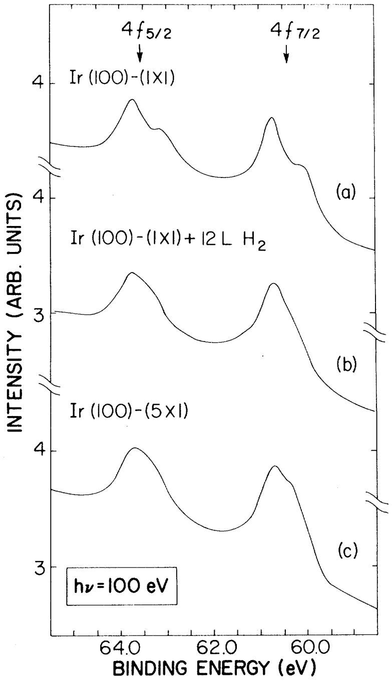

FIG. 1. Photoemission spectra of Ir $4f$ core levels for (a) Ir(100)-(1×1), (b) Ir(100)-(1×1) +12 L H_2, and (c) Ir(100)-(5×1).

Sunjic line shapes,[6] with a full width at half maximum (FWHM) of 2γ and an asymmetry parameter of $\alpha = 0.12$ [as determined by x-ray photoemission spectroscopy (XPS[7])] which were convoluted with a triangular-shaped instrumental resolution function having a FWHM of 0.3 eV. Then the FWHM 2γ, intensity ratio I_s/I_b of surface to bulk components, and the binding energy shift ΔE were varied so as to optimally fit the experimental line shape.[8] The optimum FWHM 2γ was found to be 0.4 eV, consistent with XPS measurements.[7]

Results for Ir(100)-(1× 1) and Ir(111) are shown in Figs. 2(a) and 2(b) (dotted curves). The bulk $4f_{7/2}$ binding energy relative to the Fermi level was found to be 60.7 ± 0.1 eV, in agreement with XPS measurements.[7] In order to obtain a good fit, a small background due to extrinsic energy losses was included, which at each energy was taken to be proportional to the peak area integrated from the high-kinetic-energy tail to the energy of consideration. I_s/I_b and ΔE values and their estimated errors obtained from this fitting procedure are listed in Table I.

The $4f_{7/2}$ line shape for the (5×1) reconstructed Ir(100) surface is very similar to that from the Ir(111) surface [Fig. 2(c)]. A close examination shows that the (5×1) line shape has extra structure, indicating that at least two different surface core-level binding energies are involved. An improved fit was obtained by using two surface core levels with $\Delta E = 0.44$ and 0.75 eV and $I_s/I_b = 0.83$ and 0.15, respectively. This corresponds to an average shift of $\Delta\bar{E} = 0.49$ eV and a total intensity ratio of $I_s/I_b = 0.98$ (Table I).

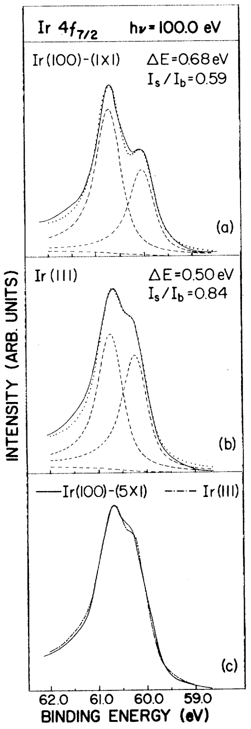

FIG. 2. $4f_{7/2}$-core-level emission spectra for (a) Ir(100)-(1×1) and (b) Ir(111) after background subtraction (solid lines) and the result of our line shape fit (dotted lines). Dashed curves show the decomposition into Doniach-Sunjic lines convoluted with the instrumental resolution; an extrinsic background is also shown. (c) Comparison between core-level emission spectra from Ir(111) and Ir(100)-(5×1).

TABLE I. Binding-energy shifts and relative intensities of $4f$ core levels from surface atoms of Ir.

Surface	ΔE[a] (eV)	I_s/I_b[b] Expt.	Calc.
Ir(100)-(1×1)	0.68	0.59	0.66
Ir(100)-(5×1)	0.49[c]	0.98[c]	0.94
Ir(111)	0.50	0.84	0.80

[a] Estimated uncertainty = ± 0.02 eV.
[b] Estimated uncertainty = ± 0.02.
[c] Average values (see text).

In general, surface core-level shifts reflect the change in electrostatic potential in the atomic core region. In Ir these are mainly due to configuration changes[3] (rehydridization, d-band narrowing, surface states, etc.). Namely, these shifts are sensitive to changes in d-electron localization near the core and especially to changes in the number of d electrons ($s/p/d$ rehybridization effects).[3] Rehybridization can differ widely for surfaces of different elements and is influenced by surface geometry, including possible surface-layer relaxation effects. At the surface, an increase in d localization can occur due both to d-band narrowing (e.g., reduced surface-atom coordination[9]) and to changes in the shape of the local density of states, which correspond to a transfer of spectral weight from the lower "bonding" portions of the d band to the upper "antibonding" portions of the d band.[10-13] It is interesting that recent self-consistent surface calculations have predicted an upward surface core-level shift of 0.5 eV for Cu(111)[11] but downward shifts of 0.22 eV and 0.48 eV for Ti(0001) and Sc(0001).[13] The sign of these calculated shifts has been attributed to the combined effects of the d-band narrowing and layerwise charge neutrality, which results in an upward shift of the d band if the Fermi level is above the midpoint of the d band and vice versa.[13] If it is further assumed that the surface core-level binding energy shifts rigidly with the d-band center of gravity,[1] this model predicts the correct sign for the surface core-level shifts seen for Au, Ir, and Ta. However, it predicts essentially no shift for W, which shows a 0.3-eV upward shift.[2]

While the use of a simple d-band tight-binding model is very questionable for predicting absolute surface level shifts, we find that it correctly predicts the relative shifts for the unreconstructed (100) and (111) Ir surfaces. In a tight-binding model, the bandwidth is proportional[9] to $\sqrt{Z}$, where Z is the atom coordination number. Given the shift ΔE_{111} for the (111) surface, the shift ΔE_{100} for the unreconstructed (100) surface follows from $\Delta E_{100} = [1-(Z_{100}/Z_b)^{1/2}]/[1-(Z_{111}/Z_b)^{1/2}]\cdot\Delta E_{111}$. Substituting $Z_b = 12$ for the bulk and $Z_{111} = 9$ and $Z_{100} = 8$ for the surfaces, we obtain $\Delta E_{100}/\Delta E_{111} = 1.37$, in excellent agreement with the experimental ratio of $0.68/0.50 = 1.36$.[14] This suggests use of core-level shifts for structural analyses of surface layers.

The $4f$ surface core-level shift for Ir(100)-(5×1) remarkably resembles that for Ir(111) [Fig. 2(c)], strongly suggesting that these surfaces have similar coordination. With use of a structural model proposed in LEED investigations, the (5×1) structure is due to a single hexagonally close-packed layer of Ir atoms on top of a (100) substrate.[15] This structure involves surface atoms in inequivalent sites with different coordination, consistent with our observation that more than one surface core level is involved. The average number of nearest neighbors for atoms in the hexagonal overlayer is approximately 8.5. The tight-binding model then predicts an average core-level-shift ratio of $\Delta E_{100}^{(5\times1)}/\Delta E_{111} = 1.18$, as compared with an experimental ratio of 0.95. The smaller observed shift indicates a more bulklike coordination, which could be due to a slight buckling of the overlayer [e.g., (5×20) reconstruction observed for Au(100)]. Such a buckling effect would contribute to the compression of ~4% in the hexagonal overlayer needed to match the (100) substrate.[15]

We use the I_s/I_b ratios at constant kinetic energy as a measure of the number of surface electrons. Duc *et al.*[2] have found $h\nu$-dependent modulations in I_s/I_b for normal emission and ascribed them to photoelectron diffraction effects. This effect is substantially reduced in our experiment by collecting photoelectrons within a large solid angle (~1.8 sr). The extended x-ray absorption fine structure (EXAFS) modulations remaining after angle averaging the diffraction effects are relatively small, typically less than ~± 5% at 40 eV above threshold.[16] In addition, Duc *et al.*[2] reported a strong enhancement of I_s/I_b for p-polarized light. We have not found such a large effect in our angle-integrated experiments for Ir, which suggests that the surface photoeffect[17] does not play a significant role at soft-x-ray photon energies. In conclusion, the intensity ratios at constant final energy for different Ir surfaces can be analyzed with a simple calculation based on inelastic attenuation of excited photoelectrons as follows. In a discrete layer model for electron escape, the surface to bulk intensity ratio is given by

$$\frac{I_s}{I_b} = \frac{N_s}{N_b}\cdot e^{N_s\sigma}(1-e^{-N_b\sigma}), \tag{1}$$

where $N_{s,b}$ is the surface (bulk) layer density (atoms/cm^2) and σ is the cross section for inelastic scattering per atom. In this model, electrons escaping from the bulk are attenuated through each bulk layer by a factor $\exp(-N_b\sigma)$ and finally attenuated through the surface layer by $\exp(-N_s\sigma)$. The only free parameter in Eq. (1) is σ, which is related to the bulk electron escape depth λ through $\lambda = 1/n_b\sigma$ (n_b is bulk atom density in atoms/cm^3). Calculated intensity ratios for Ir(100)-(1×1) and Ir(111) are in reasonable agreement with experiment (Table I) if σ is taken to be 3.7×10^{16} cm^2($\lambda = 3.8$ Å). A comparison of surface-to-bulk intensity ratios for the Ir(100)-(5×1) provides an additional test for the hexagonal overlayer model proposed for this surface. Assuming again a reduction of 4% in the lattice constant within the overlayer, it follows that $N_s = 1.69\times10^{15}$ atoms/cm^2 and $I_s/I_b = 0.94$, again in good agreement with the experimental value of 0.98 (Table I).

In summary, the measurement of surface core-level binding energies and intensities shows promise as a "site-specific" tool to study surfaces of transition metals and is particularly interesting for catalytically active stepped surfaces. Proof of this must await further systematic studies of surface core-level shifts for different elements and structural configurations.

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