[3] A. Javan and A. Sanchez, in Laser Spectroscopy, edited by R. G. Brewer and A. Mooradian (Plenum, New York, 1974), p. 11.

[4] The thin wire is about 10 μm in diameter. It is used as an antenna to couple incident ir radiation to the junction. See A. Sanchez *et al.*, J. Appl. Phys. 49, 5270 (1978).

[5] For review discussions of previous work see *Inelastic Electron Tunneling Spectroscopy,* edited by T. Wolfram (Springer, Berlin, 1978).

[6] In some contacts a change in the thin-wire tension is accompanied by a slight "walkoff" of the tungsten tip on the Ni base, causing a deviation from a smooth tuning plot as shown in Fig. 3, inset.

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Direct Observation of 4*f* Splitting between (110) Surface and Bulk Atoms of W

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With large surface-sensitivity enhancement achieved by use of *p*-polarized light, soft-x-ray photoemission spectra of 4*f* core levels from the outermost atoms of the (110) face of tungsten have been observed. High-resolution spectra show two well-separated 4*f* lines split by 0.30 eV, with the low–binding-energy peak being assigned to surface atoms. The ratio of the intensity of the surface peak to the bulk peak as a function of photon energy exhibits striking features which are tentatively explained.

It is widely recognized that surface photoemission is highly enhanced by employing *p*-polarized light. The overall emission (bulk plus surface photoemission) is also more effective than with *s* polarization.[1] The origin of this effect is the existence with *p*-polarized light of an electric field component normal to the surface which varies strongly over a distance of the order of electron escape depth.[2,3] Experimental evidence for this surface photoeffect has usually been obtained with photoyield measurements[4] and surface-state photoemission with low or moderate photon energy.[5]

In this Letter, we report angle-resolved soft-x-ray photoelectron spectroscopy data using synchrotron radiation which demonstrates an identical effect for core levels. A surface photoemission study of localized core-level excitation is promising, since separation of the bulk contribution should be clearer there than in the case of valence states. Our results do indeed permit distinguishing unambiguously surface core levels from the bulk levels. As a result, they allow us to answer in a definite way the fundamental question of whether the surface atoms experience a binding-energy shift. Since the surface atoms experience a potential different from the bulk because of a lower coordination number, their core levels are expected to be shifted if one only considers initial-state effects. However, the experimental situation is very controversial. From appearance-potential spectroscopy lower binding energies were claimed for surface atoms,[6] but this conclusion was subsequently vigorously challenged.[7] By grazing detection in order to increase surface sensitivity,[8] careful searches for surface binding-energy shifts in x-ray photoelectron spectra (XPS) of several metals led to the conclusion that such a shift does not occur.[9,19] Nevertheless, extra emission at a lower binding energy has recently been reported for low-takeoff-angle XPS of Au 4*f*,[11] although these results exhibited only an enhanced shoulder, not a distinct surface peak. In the current study, the surface-atom peak is clearly resolved from the bulk component. We also find that the ratio of photoemission intensity of surface level to bulk core level exhibits its modulations with photon energy $\hbar\omega$. These modulations may indicate light refraction and reflection effects[12] and/or, more likely, final-state scattering effects.[13-16]

The W 4*f*-level soft-x-ray photoemission spectra presented here were obtained at the Orsay colliding ring. The light was dispersed by a toroidal-grating monochromator delivering high photon flux ($\simeq 10^{12}$ photons $\text{Å}^{-1}\ \text{s}^{-1}$ at 100 eV in the energy range of 20 to 150 eV. The 127° cylindrical-type electron analyzer[17] had an angular resolution better than 1° and was operated in the constant-energy mode. The overall energy resolution (monochromator plus electron analyzer) is 0.12 eV at $\hbar\omega = 70$ eV and it decreases as the photon energy increases. The polarization of the light is changed by rotating the sample relative to the direction of the light. The W(110) face was cleaned by repeated cycles of Ar-ion bombardment, oxidation, and subsequent flashes to 2300 K performed before every measurement. The cleanliness and order of the surface were checked by Auger spectroscopy and low-energy electron diffractions; and no trace of carbon, the major contaminant of W, was detected. The base pressure was in the low 10^{-10}-Torr range.

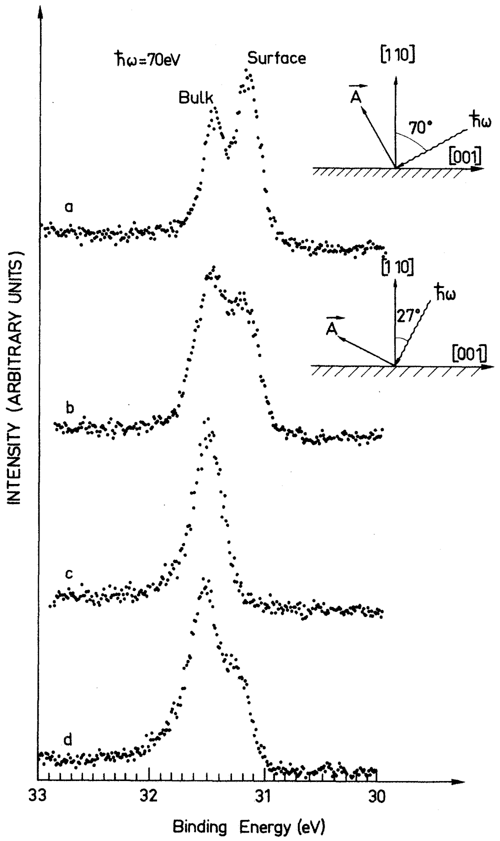

FIG. 1. Changes of the W(110) $4f_{7/2}$ spectra with polarization and contamination. Curve *a*, clean surface, *p* polarization; curve *b*, clean surface, *s* polarization; curve *c*, 10-L H_2 exposure, *p* polarization; curve *d*, 1-L O_2 exposure, *p* polarization.

Figure 1 displays different W $4f_{7/2}$ spectra recorded along the surface normal for a photon energy of $\hbar\omega = 70$ eV. Curve 1*a* represents the spectrum for the clean surface. The photons impinged on the surface at an angle $\alpha = 70°$ relative to the normal and this corresponds to an 80% *p* polarization. Two distinct and narrow peaks with average full widths at half maximum (FWHM) of 0.25 eV, appear well separated by a 0.30-eV splitting. The same splitting is found for the close-lying W $4f_{5/2}$ level. The intensity of the low-binding-energy peak relative to the high-binding-energy peak is strongly decreased from a ratio of 1.3 to 0.6 by changing the light to *s* polarization obtained at 70% with $\alpha = 27°$ (curve 1*b*). At the same time, the total intensity for both components is reduced by a factor of $\simeq 3$. An intensity decrease in the low-binding-energy peak is also obtained by exposing the surface to hydrogen or oxygen, as demonstrated in the spectra 1*c* and 1*d* recorded with *p* polarization after an exposure of 10 L (1 L = 1 μTorr sec) of H_2 and 1 L of O_2, respectively. The total absolute area of the two $4f_{7/2}$ peaks furthermore remains constant from clean to adsorbate-covered surface. The relative ratio of surface to bulk peak is found to be very sensitive to the nature and reactivity of the crystalline face.

This general behavior is clear evidence for assigning the low-binding-energy peak to surface atoms. At this stage, we emphasize that the surface core levels follow all of the usual criteria for the identification of true surface states, that is to say, enhancement with *p* polarization, sensitivity to contamination, and an energy location independent of photon energy; these conditions are of course recognized to be necessary but not sufficient.[5]

Turning now to binding energy, we conclude that surface atoms are lower in energy relative to the bulk, corroborating a previous XPS measurement.[11] We point out, however, that in our experiments the overall resolution is better and that the surface emission relative to the bulk is stronger than in this prior study, thus allowing a more direct observation of the surface-bulk shift. The lower binding energy for surface atoms was previously explained[11] by a reduction in d-sp hybridization at the surface, resulting in a more localized charge for the d band as indicated by the observation[11] of a narrower width of the density of occupied surface states, in agreement with tightly-binding calculations.[18] An alternative interpretation invoked larger polarization relaxation at the surface than in the bulk because of the coupling of the core hole with surface plasmons,[19] but this argument has been seriously questioned.[20] Crystal-field effects have also been proposed for explaining Al-$2p$ surface broadening[21] and adatom-core-level splitting.[22] At this time, more data on other faces and metals appear necessary for separating the ground-state shift from many-body final-state effects.

The line shapes for both volume and surface peaks are similar. The $4f_{7/2}$ FWHM's measured at $\hbar\omega = 70$ eV and corrected by a 0.125-eV experimental broadening are 0.19 and 0.22 eV for volume and surface, respectively. It appears then that the surface width could be slightly larger than the volume width. A possible explanation is lifetime broadening by surface-plasmon excitation as theoretically predicted in the case of free-electron metals.[23]

The photon-energy dependence of the surface $4f$ levels has been investigated in the 53–140-eV energy range. The volume-surface energy splitting remains unchanged (0.30 ± 0.02 eV) and the bulk $4f_{7/2}$-level binding energy, referred to the Fermi level, is found to be constant (31.5 ± 0.1 eV), in agreement with high-energy XPS measurements.[24] Thus, no shift of the surface peak with photon energy is detected. However, the ratio of the area of surface peak to bulk peak as a function of photon energy for both the $4f_{5/2}$ and $4f_{7/2}$ levels exhibits striking features (Fig. 2). The $4f$ surface-atom photoemission relative to the bulk shows, after a steep decrease, a prominent and sharp maximum at a photon energy of ≃ 70 eV followed by a broad peak at ≃ 110 eV.

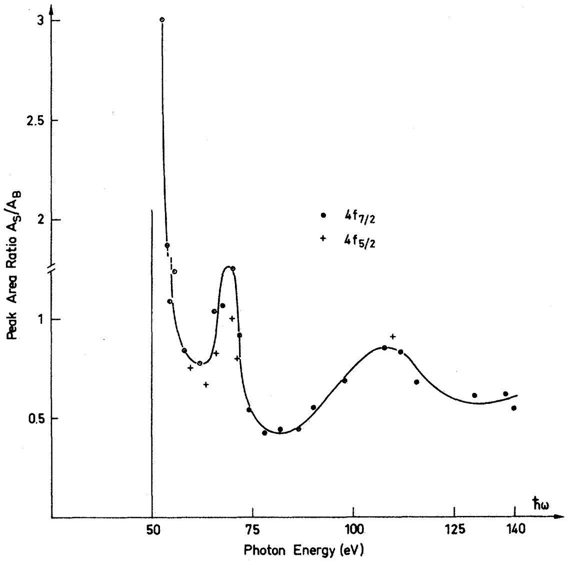

FIG. 2. Intensity ratio of surface (A_S) to bulk (A_B) peak area as a function of photon energy for W-$4f_{7/2}$ (circle) and W-$4f_{5/2}$ (plus) levels.

The surface sensitivity of XPS has been generally discussed in terms of electron mean free paths only. However, the high sensitivity to the outermost surface-atom core level in our measurements and its strong variability with $\hbar\omega$ cannot be understood with a model simply based on inelastic attenuation of exiting photoelectrons according to their kinetic energy. It is also not possible to understand the difference between surface and core-level emission for s and p polarization in this way. To explain the relative variation of surface and volume peaks as a function of $\hbar\omega$ (Fig. 2), the electron mean free path would have to increase by one order of magnitude in the kinetic energy range 20 to 110 eV, and this is inconsistent with experimental values which are found to remain constant for W in this range.[25] In any case, the intensity modulations of Fig. 2 cannot be accounted for within this scheme. Two other possible explanations can be suggested for understanding our results, namely the surface photoeffect and photoelectron final-state effects.

By sweeping the photon energy, we may induce modifications in the polarization vector $\vec{A}$ as a result of refraction and reflection effects[12] and this in turn would affect the surface photoexcitation cross section. In fact, such refraction and reflection effects have been shown to correlate fairly well in the energy range $\hbar\omega = 10$–35 eV with the photon-energy dependence of the photoexcitation cross sections for the surface resonances of W(100) and Mo(100).[26] The same origin may then be equally well proposed for explaining the photon-energy dependence of the ratio of surface to core-level photoemission of Fig. 2.

However, a more probable explanation for the exhibited intensity modulations is given by a final-state effect, namely, scattering of the photoelectrons. This has been shown to explain very accurately the azimuthal photoemission distributions of core levels from clean surfaces.[13,14] Large modulations have also been theoretically predicted in the normal emission as a function of final energy for adsorbate core levels[13,15] and this has been confirmed by experiment.[16]

Tungsten is known to be an excellent electron scatterer. Thus an appreciable fraction of the normal photoelectrons that we detect here from the surface of W(110) may have undergone single or multiple scattering from the underlying bulk layers. For the bulk peak such indirect emission channels should be more complex, perhaps tending to smear anisotropies to a degree. Therefore, the intensity ratio of the two emissions (Fig. 2) may monitor the somewhat simpler interference modulations which occur in the clean-surface core level, as for adsorbate core levels. Additional evidences supporting photoelectron diffraction effects are found in the strong azimuthal and polar anisotropies of the two emissions.

As concluding remarks, we stress the important consequences of our findings. The surface photoeffects can be observed with p-polarized light in core-level photoemission which offers a convenient means for characterizing this photoeffect, since the separation of surface and bulk contributions is more effective. The surface-atom core levels are found to be located at binding energies lower than the bulk energies. The surface core levels also behave in a manner identical to surface states, providing a fruitful and easier tool for studying chemisorption. The intensity of surface core-level emission in a normal direction shows large modulations relative to the bulk and, if this effect is dominated by final-state scattering effects as for an adsorbate, normal photoelectron diffraction could be very promising for determining the crystallography of clean surfaces.

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