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Core-Hole Lifetime and Screening are Different in the Surface of W(110)

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Abstract

High resolution 4*f* photoemission spectra from clean W(110) show that the natural lifetime width and the singularity index, which characterizes the conduction electron screening, are both larger in the first atomic layer than in the bulk. The phonon broadening of the surface and bulk components are smaller than earlier theoretical estimates. The excess broadening at the surface is compatible with a simple Debye model. These findings are very different from the interpretation previously given surface-atom core-level line shapes and have implications extending to other systems.

Introduction

In the decade since a core-electron singal from the first atomic layer of a metal was first resolved in the Au 4*f* spectrum [1], a substantial effort has been devoted to measuring the surface-atom shift in different metals and determining its dependence on surface orientation and adsorption [2]. The emphasis of theoretical work has been on relating the shift to the narrowing of the bands [3] or to the reduction of the cohesive energy at the surface [4]. Many of the experimental studies also gave clear indications that the core-electron line width of the surface signal is not the same as that from the bulk [5–8]. This is, of course, no surprise, since there are three physical processes that contribute to the line width, which may well be different in the first atomic layer. (1) The vibrational spectrum of surface atoms is different, resulting in a different phonon width. (2) The screening of the core hole by the conduction electrons may be different, resulting in a distinct line asymmetry. (3) The core-hole decay rate may be modified, if it depends on CVV Auger transitions, resulting in a different natural width at the surface. Without specific evidence to support the assumption, the broadening of the surface signal, when observed, has generally been attributed to the phonon mechanism.

Unlike the core-electron binding-energy shift, which can be obtained by inspection when the surface emission is well resolved, sorting out the three contributions to the line width requires more sophisticated techniques. It does not suffice to measure the width at half height; one must be able to characterize the line shape, because each of the three processes results in a distinctly different form of broadening. Phonon excitation results in a Poisson line shape, which is well approximated by Gaussian in the limit of a many-phonon process. Lifetime broadening has a Lorentzian shape, with tails that extend many line-widths away from the peak. Conduction electron screening contributes a distinctive, asymmetric, singular power-law line shape, which typically extends out to the plasmon satellites.

In order to obtain information about these phenomena it is necessary to compare the experimental line shape with a theoretical one which properly incorporates the physical processes responsible for the data. There is no rationale to fitting a spectrum with a mathematical function whose parameters lack physical significance. We use a functional representation in which each photoemission line is defined by five parameters directly related to physical variables: (1) the line position, related to the binding energy, (2) the amplitude, related to the photoelectric cross section and escape depth, (3) the Lorentzian width, related to the lifetime of the core hole, (4) the singularity index, related to the conduction-electron screening, and (5) the Gaussian width, related to the combined effects of the phonon width and instrumental resolution. Only the last three have bearing on the line shape. The Doniach–Šunjić (D–S) [9] equation provides a convenient expression combining the effects of the Lorentzian width and the singularity index. The Gaussian width is introduced by convolution. The background is represented as a general quadratic or cubic function of the kinetic energy. This is adequate when the range of the fit is limited, provided the photon energy is chosen to exclude plasmon and Auger peaks from the region of analysis. All parameters, including those which describe the background, are optimized by a least-squares adjustment. Background subtraction prior to the line shape analysis is ill advised, since it is impossible to separate the Lorentzian and many-body tails from the inelastic background by inspection.

In order to ensure that the results of such an analysis are meaningful, one must impose a number of conditions. A necessary condition is that the model function fit the data without leaving unexplained deviations that exceed the statistical uncertainty of the data points. If this criterion cannot be satisfied the model function does not provide a complete description of the data, and resulting output parameters are of dubious validity. However, the above condition is not sufficient to guarantee that the resulting parameters are physically meaningful. The further requirement is that there be no strong correlations between the parameters, i.e., regions in parameter space where one can obtain comparable fits while trading off one parameter for another. (Most least-squares routine provide a parameter correlation matrix as part of the output.) Strong parameter correlations, commonly encountered when fitting unresolved lines, give a clear warning that the fitting procedure is incapable of giving unique values for the correlated parameters. In fact, it is generally true that if you cannot identify the components by inspection, then the least-squares adjustment will also encounter difficulties.

Experimental details

For a first attempt to deal quantitatively with the shape of

the surface-atom core-electron spectrum we chose the W(110) surface, which does not reconstruct in the absence of adsorbates [10]. It has two other important characteristics: (1) the surface-atom core-level shift is much larger than the natural lifetime and phonon widths and the available instrument resolution, and (2) the second layer atoms have the full nearest and next-nearest neighbour coordination of the bulk atoms. This surface should consequently yield an ideally simple well-resolved spectrum, amenable to detailed analysis.

The single-crystal sample dimensions 4 × 30 × 0.25 mm was cleaned by resistive heating to 1520 K in 10^{-7} Torr of oxygen followed by flashing to 2300 K in a vacuum of 1×10^{-10} Torr. After cooling to either 210 or 310 K, which took only seconds due to the large difference in thermal mass between the sample and its mounting, photoemission data were collected using the AT&T Bell Laboratories 6 m toroidal-grating monochromator (TGM) on the VUV ring of the National Synchrotron Light Source. A 100 mm VSW hemispherical analyzer was used with a pass energy of 2 V, which corresponds to a resolution of 40 meV (FWHM). The high intensity of the monochromatized radiation (70 eV for all measurements reported here) allowed single 2.5-eV scans with good statistics to be obtained in only 4 min, a time so short that the average surface H contamination is estimated not to exceed 0.01 monolayer.

The instrumental resolution was determined from measurements of the Fermi cut-off of the W(110) crystal, see Fig. 1. The spectra were fitted with a convolution of the Fermi function (for the appropriate temperature) and a Gaussian, representing the combined effect of the TGM and the electron energy analyzer. The average value obtained from 13 spectra is 83 ± 3 meV FWHM. (The error limits quoted here and throughout the paper represent a 95% confidence level, based on deviations from the mean of results obtained from fitting a large number of independent data sets.) Subtraction of the electron analyzer width yields a photo resolution of 73 meV, which is consistent with earlier determinations based on the much sharper Fermi edge of Cu at 90 K. Analysis of both Cu and W Fermi edges confirms that the resolution function is well approximated by a Gaussian.

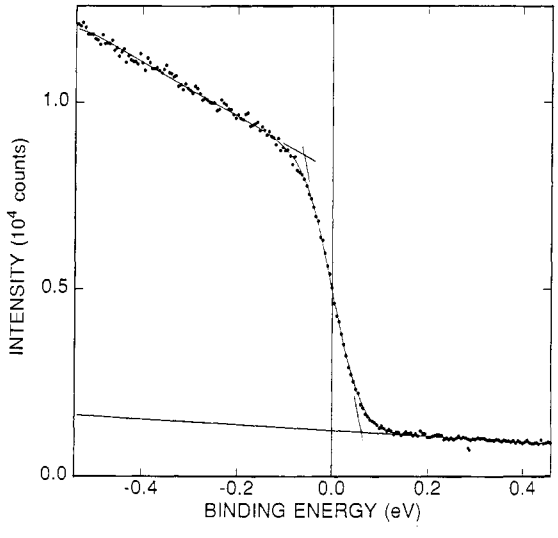

Fig. 1. The fermi edge of the W(110) surface at 210 K, taken with 70 eV photons and 40 meV electron analyzer resolution.

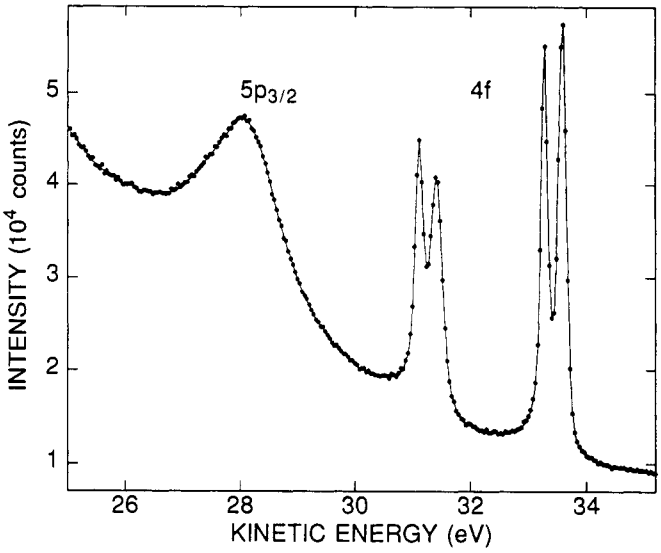

Fig. 2. Wide scan encompassing the $5p_{3/2}$ and $4f$ region of the W(110) surface, taken with 70 eV photons.

Results and discussion

A wide scan photoemission spectrum of the W $4f$ region from a freshly cleaned surface, Fig. 2, shows a broad W $5p_{3/2}$ line and two pairs of sharp lines from the W $4f$ level. The W $4f$ spin–orbit splitting of 2.16 eV is sufficiently large so that the structure of the two components can be analyzed separately. The expanded scan of the W $4f_{7/2}$ part of the spectrum, Fig. 3, shows the bulk and surface line much better resolved than in earlier studies. The solid line through the data points is the result of a fit with the model function described above. The quality of the fit is most critically assessed by the

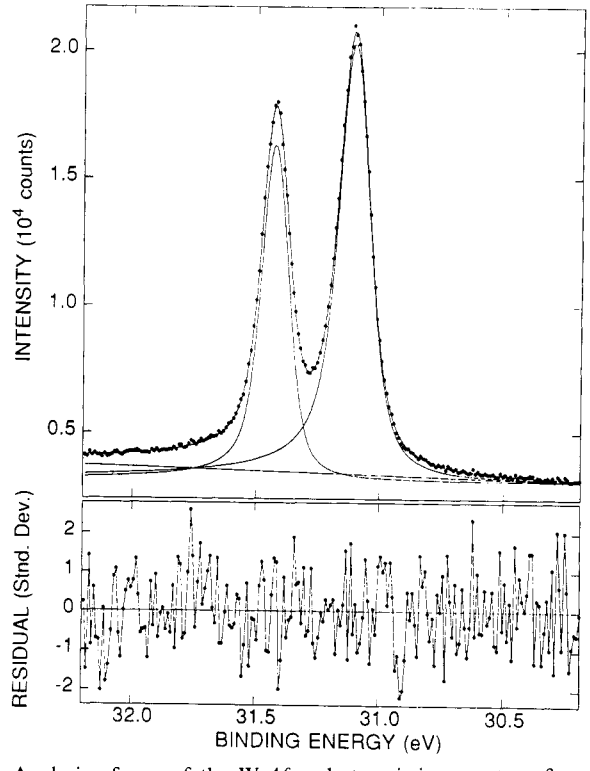

Fig. 3. Analysis of one of the W $4f_{7/2}$ photoemission spectra of a clean W(110) surface. The data, taken with 70 eV photons, are fitted with a linear background and two fully independent lines, representing the surface (right) and bulk (left) contributions. The residuals of the fit are shown in the bottom panel.

residuals plotted in units of the standard deviation in the lower panel. The majority of the points scatter randomly within a band of ± 2 standard deviations, confirming that the fluctuations are due to counting statistics. The absence of systematic deviations also shows that the model function provides a complete description of the data. Finally, parameter correlations are insignificant.

In order to demonstrate that such a fitting procedure can distinguish between Gaussian and Lorentzian broadening, we hold one or more of the width variables fixed at values away from the optimum ones obtained from the least-squares adjustment and examine the change in Chi-squared when the others are allowed to readjust in the presence of this constraint. Since the two Gaussian widths are almost the same in the optimum fit (see below), we constrain them to a common value and examine the resulting values of the Lorentzian widths and the singularity index. The results in Fig. 4 show a well defined minimum in Chi-squared, demonstrating that the Lorentzian lifetime and Gaussian phonon broadenings are readily distinguishable in these data. In a similar analysis in which the two Lorentzian widths ae constrained to a common value and the Gaussians are allowed to assume distinct values, the minimum in Chi-squared lies significantly higher.

The quality of the fit shown in Fig. 3 demonstrates that the signal from the second atomic layer cannot be distinguished from that of the bulk, i.e., the shift of the second layer must be small compared to the width of the bulk line, certainly less than 50 meV. This is not too surprising since the nearest and next-nearest neighbour coordination of the subsurface atoms

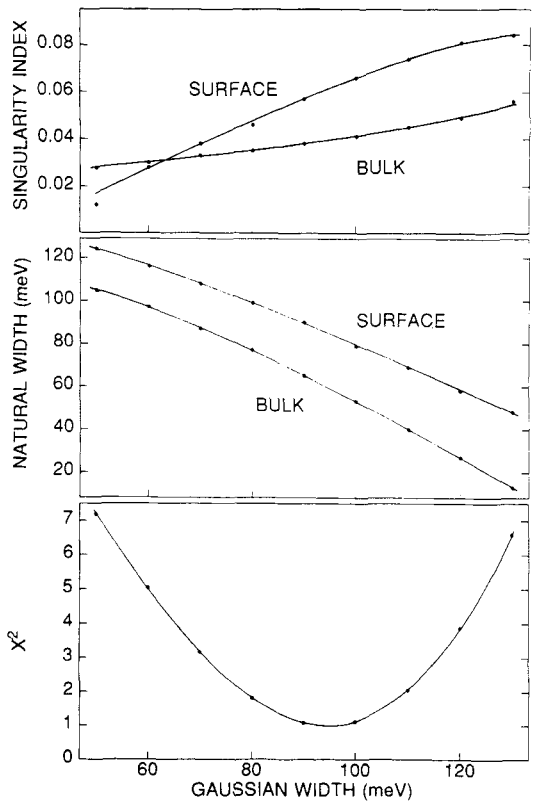

Fig. 4. Distinguishing between Gaussian and Lorentzian broadening. The bottom panel shows a cut through the Chi-squared surface of a least-squares analysis of the data in Fig. 3. The results were obtained by holding the Gaussian widths for both surface and bulk photopeaks to a common value and leaving the other parameters unconstrained. The corresponding natural Lorentzian widths and singularity indices are shown above.

are identical to those of the bulk. The relative intensity of the surface component depends strongly on both photon energy and take-off angle because of photoelectron diffraction. It is near its maximum at the conditions where the data in Fig. 2 were taken. The data, therefore, cannot be used to estimate the escape depth.

The most surprising results are the width and shape parameters obtained for the bulk and surface lines. Eighteen independent data sets were analyzed in this manner, yielding the following results:

(1) The surface atom core-level shift is -321 ± 1 meV. This value is decidedly larger than the value of 300 meV obtained from earlier data with lower resolution [11]. The (110) shift is smaller than those of the other tungsten surfaces which have been studied, 360 meV for W(100) [7] and 430 meV for W(110) [7]. The magnitude of the shift is larger for smaller numbers of nearest and next-nearest neigbours, because the width of the conduction band (which governs the shift) decreases with decreasing coordination number, but the dependence on coordination number is not linear. In a related experiment we found that this splitting is reduced by adsorbed hydrogen (initially changing by about -50 meV Langmuir^{-1} of H_2 exposure), demonstrating that great care must be exercised to maintain a clean surface during the measurments.

(2) We find that the independently determined Gaussian widths of the bulk and surface components are very similar at 210 K: 94.5 ± 2.7 and 96.0 ± 1.4 meV, respectively. At 310 K the difference is only slightly larger, 100.8 ± 4.4 meV for the bulk and 105.7 ± 1.4 meV for the surface. Subtracting the instrumental resolution in quadrature from the total Gaussian width results in an excess width for the bulk (surface) of 45.4 ± 7.6 (48.4 ± 5.5) at 210 K and 57.3 ± 8.7 (65.6 ± 4.2) at 310 K. The temperature dependence immediately identifies these widths, which are plotted in Fig. 5, as due to phonons excited during the photoemission process [12]. The room temperature values are significantly smaller than the semiempirical estimate of 109 meV [13], and both values are smaller than the theoretical estimates of 76 and 88 meV [14] for bulk W at the corresponding temperatures (also shown in Fig. 5).

Although the measured phonon broadening is less than that expected from either calculation above, the results for the temperature dependence, along with the slight difference in surface and bulk values, are both consistent with an estimate based on the bulk and surface Debye temperatures of W(110). Using the bulk width at 310 K as the reference point and a bulk Debye temperature of 310 K [15] gives the dashed line in Fig. 2. Keeping the coupling strength to the phonons constant but lowering the Debye temperature to 250 K, a value appropriate for the W(110) surface [16], produces the dot-dashed curve which just intersects the error bars on the surface data. Thus, although the difference in phonon broadening is too small to discern a statistically significant difference between the surface and the bulk, the data are consistent with a simple interpretation based on a Debye-phonon spectrum in the limit of a Gaussian line shape.

(3) In contrast to the small difference between the bulk and surface phonon broadening, the data clearly show that the core-hole lifetime width is distinctly larger at the surface. Analysis of the 18 data sets yields a width of 60 ± 3 meV for the bulk and 84 ± 3 meV for the surface. The value for the

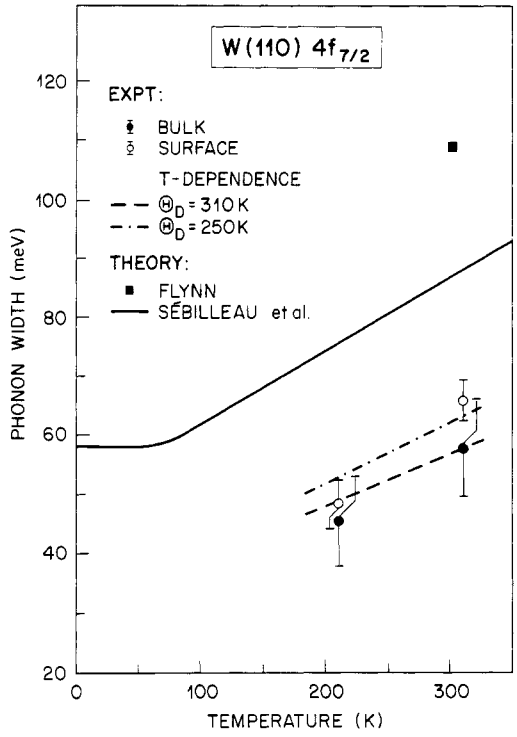

Fig. 5. Experimental phonon widths of the bulk and (100) surface W $4f_{7/2}$ levels compared with the results of various theoretical calculations.

lifetime width of the bulk line is in satisfactory agreement with earlier determinations [7], which were 55 and 61 meV. Although these widths are comparable to the theoretical value of 70 meV for the $4f_{7/2}$ level-width of the free atom [17], the differences shed some light on the mechanisms which alter the core-hole decay rate.

The transition from atom to metal has predictable effects on the $4f_{7/2}$ hole-state decay, because it proceeds almost entirely by $N_7O_{4,5}O_{4,5}$ Auger transition. (The fluorescence yield is only 7×10^{-6} [17].) The formation of the 5*d* band in the metal has two opposing effects on the Auger rate. On the one hand, the Auger rate is enhanced because the *d*-band occupancy is increased from $5d^4$ in the atom, both by reconfiguration in the initial state and by the 5*d* screening charge in the final state. On the other hand, the Auger rate is reduced by the delocalization of the 5*d* conduction electrons, which decreases the overlap between the 4*f* and 5*d* orbitals. Since the CVV Auger rate varies as $n(n-1)$, where n is the occupancy of the 5*d* band in the initial core-hole-state of the Auger process, the screening charge alone should increase the rate by a factor of 5/3. The smaller lifetime width observed in the bulk metal relative to that calculated for the free atom indicates that the effect of delocalization associated with band formation is even stronger. Conversely, the reduced delocalization in the narrowed, more atomic-like surface 5*d* band is responsible for the larger lifetime width observed in the surface. This leads to the general conclusion that the narrowing of bands at the surface will increase CVV Auger rates, increasing the width of core levels with CVV decay channels. This mechanism may account for many of the known cases of surface core-level broadening.

(4) The singularity index, α, of the bulk and surface lines are also different, 0.035 ± 0.003 and 0.063 ± 0.003, respectively. The small absolute values of α, compared to, e.g., the simple metals Na, Li, Mg and Al [12], are a consequence of the larger fraction of screening charge residing in orbitals of higher angular momentum. The bulk value of α is close to the minimum value of 1/32 obtainable for screening by *s*, *p*, *d* and *f* orbitals. Sébilleau *et al.* [14] have calculated α to be 0.075 for bulk W. Although this value is roughly twice the experimental one, their calculation does show that the D–S line shape is appropriate for W, since the valence-band excitation spectrum is approximately constant from 0 to 5 eV.

Conclusions

We have shown that the modification of the electronic properties at the surface readily accounts for the changes in the core-electron photoemission spectra from the first atomic layer of W(110). There is no anomalous phonon broadening, no evidence for crystal field splitting, and no need to postulate unresolved lines from subsurface layers. The important phenomena at the surface are the changes in the natural width and the conduction electron screening. These conclusions stand in contrast to the earlier tendancy to arbitrarily assign the surface broadening to phonon excitation. Our results consequently call for a reexamination of some or all of the earlier interpretation of surface-atom core-level widths [1, 5–8]. For example, the present findings indicate that the excess width of the surface signal from Ta and other W surfaces is due almost solely to the increased natural width of the core hole, and not the other broadening mechanisms which have been proposed. For W(111) we have confirmed that the extant data are compatible with an increase in the natural width at the surface, but the data are not of a quality to allow a determination of independent line shape parameters for the bulk and surfaces lines. It should certainly not be assumed, as has been done in the past, that the natural width is the same in the bulk and surface, especially when the core hole is subject to Auger processes involving valence electrons. In addition, the singularity index should not be assumed to be unchanged at the surface, even when the bulk value is small. The new understanding of surface effects in core-electron photoemission, combined with the higher energy resolution and beam intensities now obtainable from improved synchrotron sources and beamline optics, opens up many new directions for the surface studies.

Acknowledgements

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