Photoelectron diffraction determination of the geometry of a clean metal surface: Ta(100)

R. A. Bartynski
Department of Physics and Astronomy, Rutgers University, P.O. Box 849, Piscataway, New Jersey 08855-0849

D. Heskett*
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6396

K. Garrison
Department of Physics and Astronomy, Rutgers University, P.O. Box 849, Piscataway, New Jersey 08855-0849

G. M. Watson
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6396

D. M. Zehner
Solid State Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6032

W. N. Mei
Department of Physics, University of Nebraska–Omaha, Omaha, Nebraska 68182-0266

S. Y. Tong
Department of Physics and Laboratory for Surface Studies, University of Wisconsin–Milwaukee, P.O. Box 413, Milwaukee, Wisconsin 53201

X. Pan
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6396
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The ratio of photoemission intensities from the bulk- and surface-shifted $4f$ core levels of the clean Ta(100) surface was measured in two different modes: as a function of photon energy at normal emission and as a function of polar angle near the [011] azimuth at $\hbar\omega = 65$ eV. We have also performed a multiple-scattering photoemission calculation for several first interlayer spacings ranging from the bulk value to a 15% contraction. The best agreement with experiment was obtained for a $(10\pm5)\%$ contraction of the first interlayer spacing.

Currently, the use of photoelectron diffraction (PD) to quantitatively determine surface geometric structure has been limited to adsorbed overlayers on single crystals.[1–4] This is because the adsorbate core level provides a simple means of obtaining surface sensitivity. However, by employing surface-shifted core levels, the applications of PD could be expanded to include structural studies of clean surfaces.[5–8] This would greatly enhance the utility of this technique, while also offering several advantages over other structural probes of surfaces. The sensitivity of surface core levels to common contaminants such as hydrogen and oxygen allows the chemical state of the surface to be monitored while the geometric structure is determined by PD. With techniques such as low-energy electron diffraction (LEED) or ion scattering, such monitoring is extremely difficult. In addition, if the surface core level is shifted by either an adsorbed overlayer or the formation of an interface, PD can be used to determine the geometric structure of the underlying substrate. By this method one can easily discern whether structural changes accompany surface core-level shifts.

In this paper we describe a photoelectron diffraction experiment in which we have *quantitatively* determined the first interlayer spacing of the *clean* Ta(100) surface. The $4f$ core levels of this surface have relatively low binding energies (about 22 eV below E_F), narrow linewidths [about 0.3 eV for the bulk and 0.5 eV full width half maximum (FWHM) for the surface], and a large surface core-level shift (0.75 eV).[9] Consequently, the surface and bulk core levels are easily resolved in photoemission spectra and the ratio of their peak areas determined. Data were acquired in two modes: at normal emission as a function of photon energy and at a fixed photon energy (65 eV) as a function of polar angle near the [011] azimuth. We performed a multiple-scattering calculation for a range of first interlayer spacings. The best agreement with the experimental results was obtained for the theoretical calculation assuming a first interlayer spacing (d_{12}) of 1.49 ± 0.08 Å, which is a $(10\pm5)\%$ contraction from the bulk value. Other off-normal measurements, to be reported elsewhere, support this conclusion.[10] To our knowledge, this is the first

quantitative determination of geometric structure for a clean surface using the photoelectron diffraction technique. The results obtained here are in excellent agreement with those of a low-energy electron diffraction (LEED) study by Titov and Moritz.[11]

The Ta(100) sample was cut from a single-crystal rod (99.999% pure) oriented by Laue backdiffraction to within 0.2° of the (100) plane and spark cut. Sample preparation is discussed elsewhere.[9,10] The data were acquired at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory with the 15° toroidal-grating monochromator on the U12 beam line.[12] Monochromatized synchrotron radiation in the photon-energy range 50–150 eV was used to excite the photoelectrons. The electrons were collected by a 25-mm mean radius hemispherical electron-energy analyzer[13] with an angular acceptance of ±2°. The analyzer was mounted on a two-axis goniometer so that the polar angle (measured from the surface normal) and azimuthal angle (referenced to the crystallographic directions of the surface) of the detected photoelectrons could be varied independently. Experimental constraints dictated an azimuthal angle 15° away from the [011] azimuth. In all the spectra reported here, the **A**-vector of the light and the electron analyzer were in the plane formed by the incident radiation and the surface normal. The total-energy resolution of the apparatus (electrons plus photons) ranged from 0.1 to 0.5 eV over the photon energies spanned in this study.

Theoretical calculations of the angle-resolved photoemission cross sections of the Ta $4f$ levels were performed within a multiple-scattering formalism.[3] The initial state was determined for a Ta cluster using the $X\alpha$ scattered-wave method. The final state was written in terms of a multiple-scattering T matrix which propagates the photoelectron through the crystal and out of the surface. Photoelectric excitation matrix elements were calculated within the dipole approximation where only the $(l+1)$ and $(l-1)$ channels contribute. The potential sensed by the photoelectron was determined by an augmented-plane-wave (APW) calculation which assumes spherical averaging within the muffin-tin approximation. Strong inelastic scattering led to a mean free path of about 4.5 Å at an electron energy of 100 eV so that only the emission from the first three atomic layers had a significant contribution to the photocurrent. To obtain the theoretical surface to bulk-intensity ratio, the flux from the surface layer was divided by the sum of the fluxes from the second and third layers. The first interplanar spacing was the only surface structural parameter which was varied. Multilayer oscillatory relaxations were not considered and all other parameters were assigned their bulk values.

In this study, the ratio of the surface and bulk $4f$ core-level areas was determined for each spectrum, thus eliminating the need for normalization to the incident photon flux or the electron-analyzer transmission function. Other studies[5–8] employing such intensity ratios have been unable to quantitatively determine surface geometric structure. Although we are taking the ratio of photoelectron features occurring at slightly different kinetic energies, no structure in the calculated or measured results varied on an energy scale as small as 0.75 eV. Furthermore, using intensity ratios eliminates the necessity of assuming a form for the atomic cross section.

Figure 1 shows several normal-emission photoelectron spectra in the binding-energy region of the Ta $4f$ levels. In each spectrum, four large, well-resolved peaks are observed. These are the $4f_{7/2}$ bulk and surface, and the $4f_{5/2}$ bulk and surface core levels of Ta(100) occurring at binding energies of 21.7, 22.4, 23.6, and 24.3 eV, respectively. To quantitatively determine the surface- to bulk-intensity ratio, the following procedure was used: A linear background due to secondary electrons was subtracted from each spectrum and the area of each peak was determined by a least-squares fit to a Gaussian line shape and the surface- to bulk-ratio calculated. A typical background is illustrated by the dashed line in the 57-eV curve of Fig. 1. In a detailed study of Ta(100), Spanjaard *et al.*[9] performed a careful examination of the $4f$ core

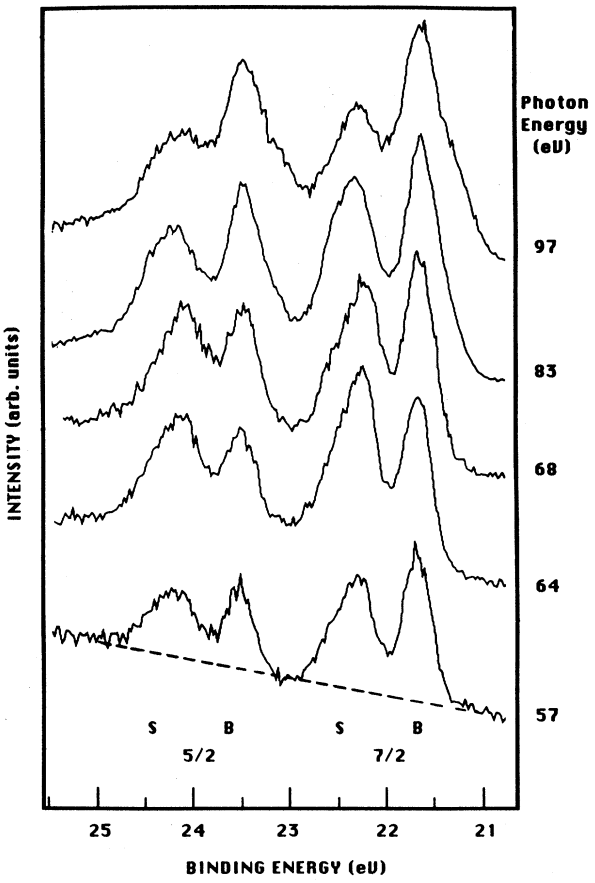

FIG. 1. Normal-emission angle-resolved photoemission spectra from Ta(100) in the binding-energy region of the $4f$ levels obtained at several photon energies with the light incident at 60° from the surface normal. The bulk- and surface-shifted peaks (B and S, respectively) are clearly resolved for each of the spin-orbit-split components in each spectrum. The dashed line in the 57-eV spectrum illustrates a typical linear background assumed for the secondary-electron spectrum.

levels, fitting each core with a Doniach-Šunjić line shape. We found that assuming a simple Gaussian form did not significantly change the surface- to bulk-intensity ratio.

In Fig. 2, the experimentally determined $4f_{7/2}$ (open squares) and $4f_{5/2}$ (solid squares) surface- to bulk-intensity ratio (vertical scale) at normal emission is plotted as a function of photon energy. The data show a minimum near 55 eV followed by a sharp maximum at 65 eV. This main peak at 65 eV is the most pronounced feature observed in this data. Above $\hbar\omega=65$ eV, the ratio exhibits an overall decrease with a broad maximum at 83 eV and a valley at 95 eV. This is followed by two broad but distinct peaks at $\hbar\omega=105$ and 125 eV. The solid lines in Fig. 2 are the theoretically predicted ratios of the surface- to bulk-intensity at normal emission obtained from the multiple-scattering calculation. The calculation was performed for a series of first interlayer spacings ranging from the bulk value ($d_{12}=1.6550$ Å) to 15% contraction ($d_{12}=1.4068$ Å) in 5% (0.0828 Å) increments.

By comparing the normal-emission data to the four theoretical calculations shown in Fig. 2, we find that the best agreement is obtained for the calculation assuming that $d_{12}=1.4894$ Å, corresponding to a 10% contraction of the first interlayer spacing. This calculation correctly predicts the large maximum occurring at 65 eV. In addition, the smaller features seen at higher photon energies occur in this theoretical curve. The peak at 83 eV and the minimum at 95 eV are somewhat stronger in the experimental data, but the energy positions of all the features are correctly predicted. Although large peaks appear in the $d_{12}=1.5723$ and 1.4068 Å calculations, they occur at somewhat different energies than those observed in the experiment. Furthermore, the next feature is seen at $\hbar\omega=77$ eV in the $d_{12}=1.5723$ Å calculation, and at $\hbar\omega=90$ eV for the $d_{12}=1.4068$ Å calculation. In contrast, this feature occurs at 83 eV in both the data and the $d_{12}=1.4894$ Å calculation. In addition, there is poor agreement between higher-energy experimental features at 105 and 125 eV and these other calculations. From the considerable disagreement between the experimental data and the calculations assuming only a 5% difference from $d_{12}=1.4894$ Å, we estimate that the Ta(100) surface is contracted $(10\pm5)\%$.

In Fig. 3 we show the experimental surface- to bulk-intensity ratio for both the $4f_{7/2}$ and $4f_{5/2}$ core levels plotted as a function of polar angle for $\hbar\omega=65$ eV, the energy of the maximum in Fig. 2. The data exhibit a large, sharp peak at normal emission. The narrow angular spread of this feature permitted alignment of the analyzer to within 1° of the normal for the energy-dependent measurement. Away from normal, a second maximum occurs near 32° with a gradual increase in the intensity ratio at larger angles. A small shoulder also occurs near 15°. The solid lines in this figure are the result of the multiple-scattering calculation for 5%, 10%, and 15% contractions. These calculations show less sensitivity to interplanar spacing; however, the results for 10% contraction show best agreement with the data. The large feature at normal emission as well as the second maximum near 32° are well reproduced by the calculation. Even the shoulder at 15° is seen. We attribute the more rapid increase of the calculated ratio at larger angles to an underestimate of the mean free path. The

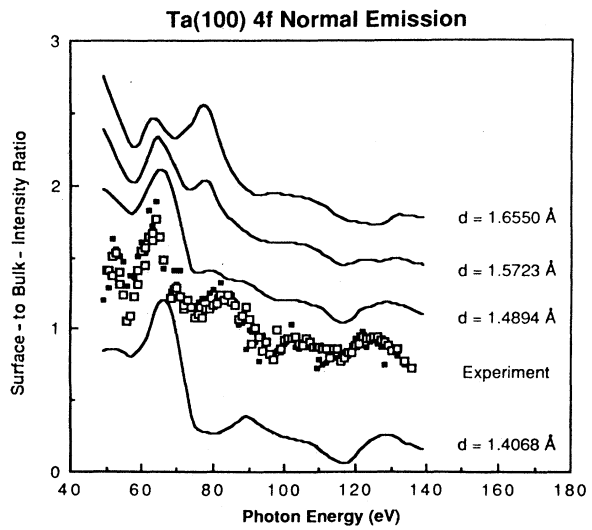

FIG. 2. The ratio of the photoemission intensity of the bulk- and surface-shifted $4f_{7/2}$ (open squares) and $4f_{5/2}$ (solid squares) core levels at normal emission (cf. Fig. 1). The vertical scale refers to the experimentally determined ratio. The solid curves are the results of a multiple-scattering calculation assuming different first interplanar spacings. The calculations were multiplied by a factor of 0.4 to appear on the same scale as the data.

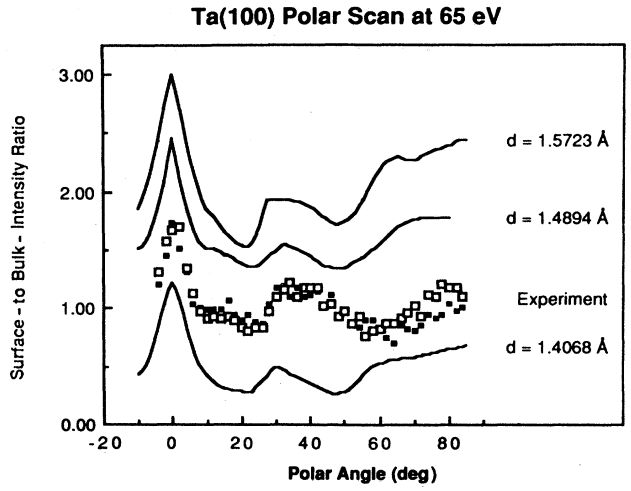

FIG. 3. The surface- to bulk-intensity ratio of the $4f_{7/2}$ (open squares) and $4f_{5/2}$ (solid squares) core levels as a function of polar angle in a plane 15° off the [011] azimuthal direction. The light was incident at 60° from the surface normal. The **A** vector and the electron analyzer in the plane defined by the incident radiation and the surface normal. The solid curve is the result of a multiple-scattering calculation assuming a 10% contracted first interplanar spacing. The calculations were multiplied by a factor of 0.4 to appear on the same scale as the data.

good agreement between these data sets and the $d_{12}=1.4894$ Å calculations, obtained for two different experimental modes, provides strong evidence in support of a 10% first interlayer contraction.

The only other published structural study of the Ta(100) surface is a LEED study by Titov and Moritz.[11] Measured *I-V* curves for six inequivalent beams were compared to calculated spectra where both the first and second interlayer spacings were allowed to vary. A minimum reliability factor of 0.21 was obtained for an 11% contraction of the first interlayer spacing accompanied by a 1% expansion of the second interlayer spacing. In our calculation, only the first interlayer spacing was allowed to vary and our result of a (10±5)% contraction agrees with the LEED study well within the estimated errors of each experiment. In addition, the results from calculations of surface core-level shifts (SCS)'s are also consistent with a first interplanar contraction. Spanjaard *et al.*[9] calculated a SCS of 0.9 eV for Ta(100) using a tight-binding method to determine the local valence-band density of states at the first atomic layer. By adding spin-orbit coupling and a 10% contraction, this was reduced to 0.8 eV, improving agreement with experiment. In a slab calculation of Ta(100), performed by Krakauer[14] within a surface linearized augmented-plane-wave (LAPW) framework, a SCS of 0.95 eV was obtained for the unrelaxed surface. It was pointed out in the discussion of those results that the assumption of a bulk value for the first interplanar spacing may account for this overestimate of the SCS.

In conclusion, we have adapted the technique of photoelectron diffraction to study the geometry of a clean metal surface. Application of PD to clean surfaces allows one to simultaneously monitor surface cleanliness and surface core-level shifts while determining surface geometry. By comparing the energy dependence of the surface- to bulk-intensity ratio of the 4*f* core levels to a multiple-scattering calculation, we have quantitatively determined the first interplanar spacing of the clean surface of Ta(100). It is found that $d_{12}=1.49\pm0.08$ Å corresponding to a contraction of this spacing by (10±5)% compared to the bulk value. This spacing is consistent with that found in a LEED study by Titov and Moritz.[11] Further experiments to determine the first interlayer spacing of the hydrogen-covered Ta(100) surface and other 4*f* metals are underway.

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*Permanent address: Department of Physics, University of Rhode Island, Kingston, RI 02881.

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