# Photoemission Observation of a Surface State of Tungsten

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Photoelectron energy distributions from clean, polycrystalline tungsten reveal a surface-sensitive peak about 0.4 eV below the Fermi energy. This peak, which is identified as a surface state, rapidly decays during gas adsorption, and concomitant growth of a new peak at ~2.5 eV below the Fermi energy is observed. Over the energy range of the surface-state peak, the strength of surface-state emission relative to bulk emission decreases with increasing photon energy. These results quantitatively substantiate existing field-emission data and qualitatively agree with model photoemission calculations.

Recently, Forstmann, Pendry, and Heine[1] predicted surface states, or surface resonances, on metal surfaces by revising and extending Goodwin's[2] theoretical approach. Definitive observations of surface states by electron-emission spectroscopy are extremely rare for either metals[3] or semiconductors.[4-6] Field-emission energy-distribution studies have revealed surface states on clean (100) tungsten.[3] Stern[7] calculated the effect of these electronic surface states on the optical properties, and Schaich and Ashcroft[8] predicted that these states should significantly contribute to the photoyield, thereby creating surface-sensitive structure in the photoelectron energy distribution. This Letter reports the first observation of a metallic surface state in a photoemission experiment.

A polycrystalline tungsten sample was mounted so that its front surface was in the equatorial plane of a triple-grid, hemispherical, retarding potential analyzer. The vacuum chamber was capable of an ultimate pressure of ~$2 \times 10^{-11}$ Torr but, because no window materials are used between the gaseous-discharge light source and monochromator, and between the monochromator and vacuum chamber, base pressures ~$5 \times 10^{-11}$ to $1.5 \times 10^{-10}$ Torr are more typical with the light source in operation.[9] The polycrystalline sample was heat treated in $O_2$ for 100 h to remove carbon.[10] The extensive heat treatment probably reconstructed the sample to produce a predominantly (100) orientation of the crystallites.[11] Prior to measurement of an energy distribution, the sample was cleaned by Ohmic heating (5 sec at ~2700 K).

Vacuum ultraviolet (VUV) radiant energy from the capillary discharge lamp was dispersed by a near-normal incidence monochromator and was directed through the energy analyzer grids to be incident 45° to the sample normal. Elec-

trons photoemitted within a solid angle of ~0.2 sr about the sample normal struck the first dynode of an electron multiplier. The individual electron pulses were amplified, then stored in a multichannel analyzer, whose channel address generated the retarding potential. The analyzer was programmed to obtain the energy distribution, in effect, by taking the differences between adjacent channels.

Figure 1(a) displays a series of energy distributions at a photon energy of 7.7 eV, as a function of exposure to hydrogen from the VUV light source. The pressure was $1.5 \times 10^{-10}$ Torr and the exposure was calculated from the time when the energy sweep crossed the peak at $-0.4$ eV. Each sweep required about 2 min so that the exposure at lower energies is slightly less than near the Fermi energy. All of the energy distributions are plotted as a function of the initial-
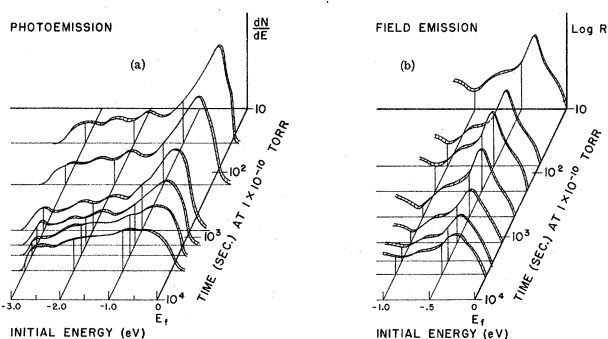


FIG. 1. (a) A family of photoemission energy distributions at $\hbar\omega = 7.7$ eV as a function of exposure to hydrogen. Each energy distribution is plotted as a function of the energy of the initial state. The energy is measured from the Fermi energy. The surface state peak is at $-0.4$ eV. (b) A family of analyzed (Ref. 12) field-emission energy distributions as a function of exposure to hydrogen. Energy is measured from the Fermi energy. Log$R$ is related to the local density of states at the surface.

state energy, i.e., plotted versus $-\hbar\omega + \varphi_e + E$, where $E$ is the kinetic energy of the photoemitted electron, $\hbar\omega$ the photon energy, and $\varphi_e$ the work function of the emitter. Figure 1(a) demonstrates the sensitivity of the peak 0.4 eV below the Fermi energy to hydrogen exposure. This peak has already decayed to a shoulder at a measured exposure of $\sim 10^{-7}$ Torr sec, or approximately 0.2 of a monolayer.[13]

Plummer and Young[14] observed the surface sensitivity of this peak in field-emission energy distributions from (100) tungsten. Plummer and Gadzuk,[3] Lea and Gomer,[15] and Gadzuk,[16] interpreted this structure as arising from a surface state existing in a spin-orbit–split gap in the ⟨100⟩ direction of tungsten. Figure 1(b) is the effect of hydrogen exposure on the field-emission energy distributions.[12] Within the range of error introduced in the exposure by using two different vacuum gauges, these curves display identical properties as a function of exposure. In particular, the peak height decreased linearly as a function of coverage with no shift in peak position. The point is that this structure (0.37 eV below the Fermi energy), and its disappearance upon adsorption, have been observed both in field emission and in photoemission energy distributions, and thus is not an artifact of either measurement process.[17] However, the 0.6-eV width of the surface-state peak observed with photoemission differs considerably from the 0.3-eV width for field emission. The increased width of the photoemission peak is too great to be caused by the analyzer resolution, but possibly could be a consequence of (1) the larger collection solid angle in photoemission as compared to field emission, (2) the degree of polycrystallinity of the sample,[11] or (3) interaction of a localized hole with the different final states for ejected electrons in the two processes.

Once the peak 0.4 eV below the Fermi energy has tentatively been identified as a surface state, one would like to utilize the capabilities of photoemission to measure the following properties of a surface state, which are inaccessible in a field emission measurement: (1) the penetration depth of the surface state, (2) the surface-state electron density per surface atom, and (3) the charge redistribution due to the destruction of the surface state. The remainder of this Letter will describe our attempts to measure these properties of a surface state from the energy distribution.

The surface-state penetration into the bulk could potentially be determined by measuring the strength of the surface-state emission relative to the bulk emission as a function of photon energy. The hot-electron attenuation length is a function of energy, decreasing with increasing energy above the Fermi energy up to at least 50 eV.[18] This is usually interpreted to mean that as the photon energy is increased the surface structure in the energy distribution will be accentuated.[5] This conclusion is implicitly based on the assumption that the surface optical excitations have the same probability as the bulk for all photon energies; however, the validity of this assumption is not general. E.g., we measured the yield from the surface state relative to the bulk as a function of photon energy. At each photon energy we examined the differences between "clean" energy distributions and those obtained after saturated adsorption of each gas. The area difference under the curve between $-1$ and $+0.3$ eV of the "clean" and "contaminated" energy distributions was taken as being proportional to emission from the surface state. For the same energy region the area under the energy-distribution curve after adsorption was assumed to represent the bulk emission. The ratio of the surface-state emission to the bulk emission (as defined above), $Y_R(\hbar\omega)$, is plotted as a function of photon energy in Fig. 2. It is apparent that with increasing photon energy the relative strength of the sur-
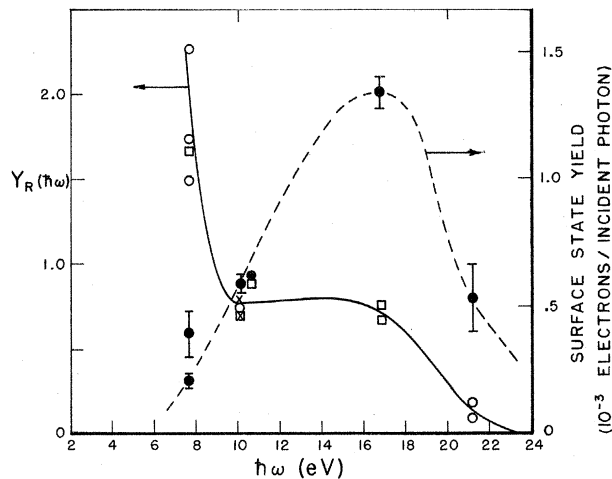


FIG. 2. The left-hand ordinate is the yield $Y_R(\hbar\omega)$ of the surface state relative to the bulk (see text) for several photon energies. The experimental points are crosses for hydrogen, open circles for oxygen, and squares for CO. The right-hand ordinate is the absolute yield of the surface state (closed circles) as a function of photon energy. The solid and dashed lines between measured points indicate the potential continuous variation with photon energy.

face-state peak decreases, whereas a hot-electron attenuation-length argument would predict an increase. This implies that the variation of the optical excitation probability with photon energy for the surface state differs from that of the bulk. Even if we knew the energy dependence of the hot-electron attenuation length, we could not separate the surface-state penetration depth and the optical excitation probability. Therefore, with existing data we are basically unable to calculate either the surface-state penetration depth or its charge density.[6]

It is also of interest to calculate the absolute yields of electrons per incident photon from the surface state. Energy distributions at various photon energies were combined with the measured yields from tungsten[9] to derive a normalization of each energy distribution and consequently the absolute yield from the surface state. The problem is that the sample formerly used for measuring the tungsten yield[9] was probably not clean enough to have the full surface-state peak height present. We will demonstrate later that the removal of the surface state, in first order, is offset by the addition of a new peak 2.5 eV below the Fermi energy. This means our yields will not be very seriously in error, except perhaps at 7.7 eV, where the − 2.5-eV peak is too close to threshold. At 7.7 eV the energy distributions were normalized using both the clean and slightly exposed surface condition to estimate this error. Figure 2 is a plot (right-hand ordinate) of the calculated absolute yield from the surface state as a function of photon energy. The two points at 7.7 eV result from the different normalization techniques described above. The surface-state yield peaks near 16 eV incident photon energy with a maximum yield of ~ 10⁻³ electrons per incident photon.

Finally, an apparent charge redistribution accompanying the destruction of the surface state will be illustrated. Figure 3 is a family of energy distributions as a function of exposure to CO at a photon energy of 10.2 eV. As the surface state peak at − 0.4 eV is removed, a new peak at − 2.5 eV appears. Surprisingly, this peak appears at the same energy for all the adsorbates we have studied ($H_2$, $O_2$, $N_2$, and CO), and therefore appears to be a characteristic of the substrate. The amplitude of this peak depends upon the gas being adsorbed. There are always energy levels characteristic of the particular adsorbate, for instance a level at − 6.5 eV for oxygen, a − 3.5-eV peak for CO adsorption, and a narrow,
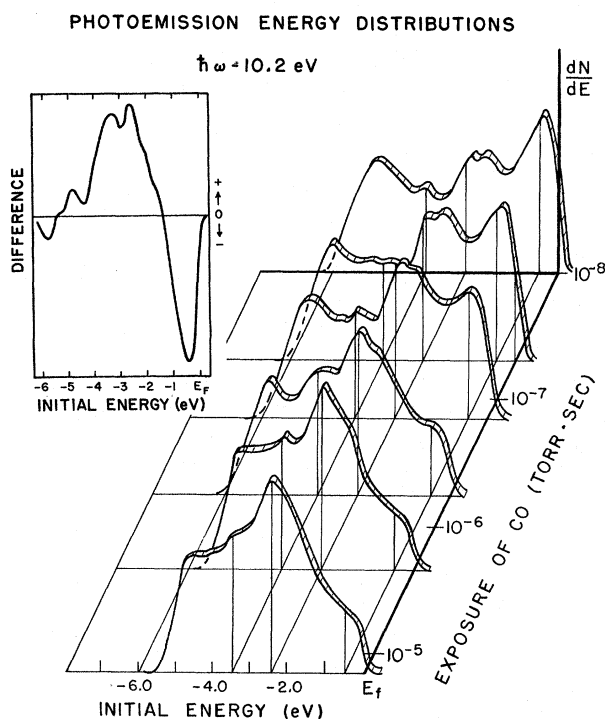


PHOTOEMISSION ENERGY DISTRIBUTIONS

FIG. 3. A family of photoemission energy distributions at $\hbar\omega$ =10.2 eV as a function of exposure to CO. As the surface state disappears with increasing exposure a new state at − 2.5 eV increases in intensity. The "clean" (lowest exposure) energy distribution was subtracted from that at $5 \times 10^{-7}$ Torr sec CO to obtain the difference curve shown in the inset.

weak peak at − 1.0 eV for low exposures of hydrogen,[12] but none of these levels is strong enough to cause the observed two-fold increase in − 2.5-eV peak height for CO adsorption compared to oxygen adsorption. It is possible that the changes in the electron escape probabilities[19] due to the various adsorbates could contribute to these differences.

The nature of the − 2.5-eV peak and its causal relationship to the surface state cannot at present be established. There are at least two possible explanations. As the surface state is removed by the adsorbate, a new localized level at − 2.5 eV is created whose charge has been transferred from the original surface state. On the other hand, it could be that the existence of the surface state creates a depletion of charge in a bulk $d$-band peak at − 2.5 eV. This charge depletion would have to occur within about one hot-electron attenuation length from the surface. Upon adsorption, the decay of the surface state would be accompanied by the refilling of depleted bulklike states near the surface. This, of course, would

imply that the adsorbate-covered surface would
yield measurements more representative of bulk
states than would the clean surface!

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# Photoemission from Surface States on Tungsten

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Energy distribution spectra of photoelectrons emitted normal to a (100) plane of tung-
sten show a pronounced peak located 0.4 eV below the Fermi level, which is attributed
to surface states. It is very sensitive to gas adsorption and disappears as the surface
is saturated with hydrogen in the $\beta_2$ state, corresponding to a coverage of $2.5 \times 10^{14}$ mole-
cules/cm$^2$.

Recently, Forstmann and co-workers[1,2] have
proposed the existence of surface states on $d$-
band metals due to the crossover of $d$ and $s$ bands
of the same symmetry. Experimental evidence
for such surface states was based on measure-
ments from photoemission spectroscopy on Ni
and Cu.[3] Recently, this evidence has been re-
futed by Eastman,[4] who pointed out that the ob-
served peaks are due to extrinsic contamination
effects rather than intrinsic surface states. In
this Letter we show that intrinsic surface states[5]
on a tungsten (100) surface are observable by
photoemission spectroscopy. Band-structure cal-
culations on tungsten,[6-8] including spin-orbit split-

ting along the (100) direction, show two band gaps
due to the crossover of $d$ bands of the same $\Delta_7$
symmetry. The present results show surface
states in only one of those gaps, while a field-
emission measurement by Plummer and Gadzuk[9]
shows two peaks attributed to surface states.
The present measurements were performed on a
(100) surface of a tungsten single crystal. Photo-
electron energy distribution spectra were mea-
sured for photoelectrons emitted normal to the
crystal surface within an angle of about 12°.
Spectra taken from a clean surface exhibit a
strong peak due to electrons emitted from a level
0.4 eV below the Fermi level, which can be at-