

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 tungsten 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 β_2 state, corresponding to a coverage of 2.5×10^{14} molecules/cm².

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 measurements from photoemission spectroscopy on Ni and Cu.³ Recently, this evidence has been refuted by Eastman,⁴ who pointed out that the observed peaks are due to extrinsic contamination effects rather than intrinsic surface states. In this Letter we show that intrinsic surface states⁵ on a tungsten (100) surface are observable by photoemission spectroscopy. Band-structure calculations 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 Δ_7 symmetry. The present results show surface states in only one of those gaps, while a field-emission measurement by Plummer and Gadzuk⁹ shows two peaks attributed to surface states. The present measurements were performed on a (100) surface of a tungsten single crystal. Photoelectron energy distribution spectra were measured 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-

tributed to surface states. The peak is extremely sensitive to hydrogen adsorption. It disappears with a hydrogen coverage of 2.5×10^{14} molecules/cm², corresponding to one hydrogen molecule in four tungsten surface atoms. This coverage is known to be the saturation coverage for the β_2 hydrogen adsorption state.¹⁰⁻¹²

The crystal used in this experiment was mechanically polished and electropolished. Cleaning took place in a low-energy electron diffraction (LEED) Auger system by heating in oxygen for several days, until no carbon could be observed diffusing to the surface. The crystal was then transferred into the experimental chamber, where an additional oxygen treatment took place. After removal of the oxide layer, cleanliness and structure was checked *in situ* by Auger spectroscopy and LEED. The pressure in the system was kept at about 1×10^{-10} Torr during the measurements. Scanning time was about 200 sec for one spectrum, so the exposure was kept below 0.02 L during a scan ($1 \text{ L} \equiv 1 \times 10^{-6}$ Torr sec, a Langmuir). A clean surface was restored by flashing to 2400°C. Photoelectron energy distribution spectra were measured using a 127° electrostatic analyzer similar to a type described earlier.¹⁸ A sketch of the experimental arrangement is shown in Fig. 1. A hemicylindrical screen of 7 mm radius ensures a field-free region around the sample S. The entrance slit of the analyzer A has been replaced by a hole of 1.5 mm diam, which, together with 40 mm radius of curvature of the analyzer, limits the resolution to about 2%. A laser beam provided a means of aligning the sample surface normal to the analyzer axis to within 1° by autocollimation. This arrangement permitted only those electrons emitted normal to the sample, within a cone of 12° opening angle, to enter the analyzer. The reason for

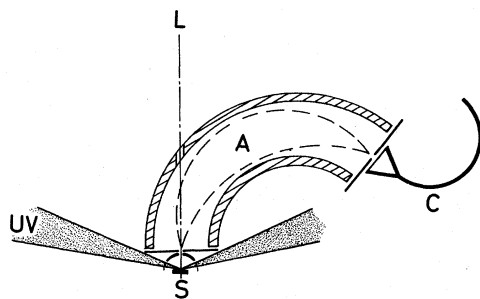


FIG. 1. Energy analyzer for photoelectrons emitted normal to a sample S. Laser beam L is used for setting sample surface normal to analyzer entrance axis. U. V., exciting light; C, channeltron.

this restriction was to exclude most photoelectrons with \vec{k} components parallel to the surface, thereby avoiding broadening of the observed surface states due to dispersion. Light was focused onto the sample forming an image of about 0.5 mm \times 1 mm, with an opening angle of roughly 25° at nearly grazing incidence.

Curve A of Fig. 2 shows the energy distribution of photoelectrons emitted normal to a clean (100) surface of tungsten. The spectrum was taken at 10.2 eV photon energy. A pronounced peak is observed centered at -0.4 eV with an emission about 6 times higher than in the rest of the spectrum. The width of the peak at half height is about 0.5 eV. This structure has been observed throughout the available photon energy range from 7.7 to 11.7 eV with approximately the same magnitude and position relative to the Fermi cut-off, which indicates that the peak is due to emission from a high density-of-states region located 0.4 eV below the Fermi level. This conclusion is supported by the fact that a similar peak has been observed in field emission experiments by Swanson and Crouser^{14,15} at -0.35 eV and by Plummer and Young¹⁶ at -0.37 eV. This peak has been assigned to surface states by Plummer and Gadzuk⁹ on the basis of its sensitivity to surface contaminants. Another peak at -1.5 eV was observed by field emission⁹ and also assigned to a surface state. The latter peak has not been observed in the present experiment.

The prominent structure observed at -0.4 eV in photoemission spectra is found to be extremely sensitive to adsorbed gases. With hydrogen ex-

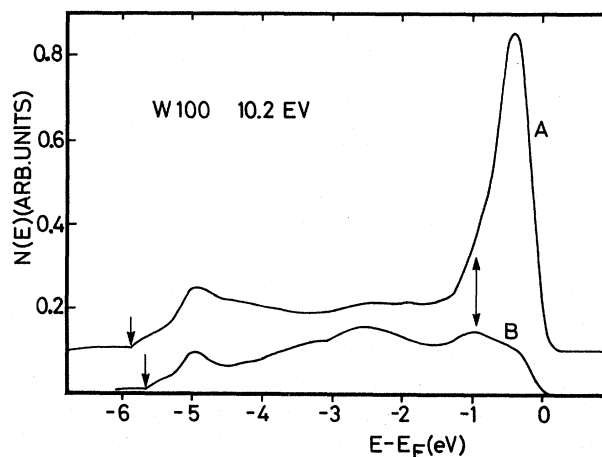


FIG. 2. Energy distribution of photoelectrons emitted normal to a tungsten (100) face at 10.2 eV photon energy. Curve A, clean surface; curve B, exposed to 0.24×10^{-6} L of hydrogen.

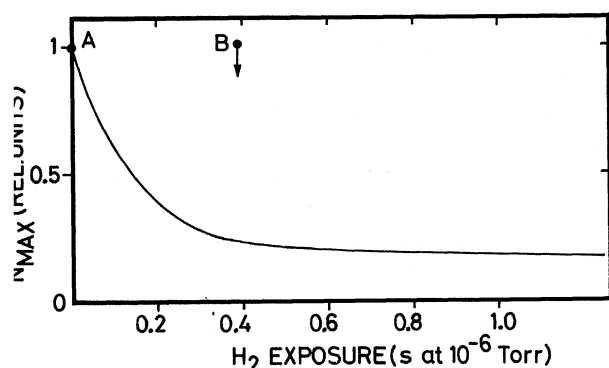


FIG. 3. Decay of the surface-state peak in photoemission with exposure to hydrogen. Photon energy, 10.2 eV. Spectra in Fig. 1 are taken at the points marked A and B.

posures of a hundredth of a Langmuir it starts decreasing and disappears completely at coverages of a fraction of a monolayer. This behavior is shown in Fig. 3, where the relative height of the peak is plotted against exposure. At an exposure of 0.39 L an energy-distribution spectrum was recorded, which is shown as curve B in Fig. 2. This curve is shown on the same scale as curve A but shifted vertically for clarity. The strong peak assigned to surface-state emission is not observed any more at this exposure, while the other features of the spectrum are preserved; for example, the structure at -5 eV. In agreement with Plummer and Gadzuk,⁹ a small peak (marked by the double arrow) is observed at about -0.9 eV, which is not affected by the exposure. It is not clearly resolved in curve A because of the intensity of the strong surface-state emission.

A work-function difference of 0.2 eV is observed from the width of the spectra, as shown by the arrows near -6 eV. This work-function difference permits the absolute coverage to be estimated, using the relations between work function and hydrogen coverage measured by Estrup and Anderson¹⁰ or Madey and Yates.¹² A coverage of about 2.5×10^{14} molecules/cm² is obtained and a sticking coefficient of 0.23 is derived from this, which is close to the value of 0.22 found by Tamm and Schmidt and the value of 0.29 observed by Adams and Germer.¹⁷

It seems surprising that a coverage of only 2.5×10^{14} molecules/cm² is so effective in suppressing the photoemission from the surface states. A possible answer is provided by the results of studies of hydrogen adsorption on tungsten by LEED^{10,17} and flash desorption.^{11,12} It has been

shown that hydrogen adsorbs on the W(100) surface in two states labeled β_1 and β_2 . The latter saturates at 2.5×10^{14} molecules/cm². In this state the hydrogen is adsorbed in atomic form^{10,11} and forms a $c(2 \times 2)$ superstructure.^{10,17} Tamm and Schmidt¹¹ have shown, in a very pictorial model, that this can be explained by assuming that the hydrogen 1s electron hybridizes with those tungsten 5d electrons that give orbitals with t_{2g} symmetry. The t_{2g} electrons form one of the d bands with Δ_7 symmetry, which are responsible for the splitting that allows the surface states discussed above.

While it is not at all certain that the calculation by Forstmann, Pendry, and Heine^{1,2} for the case of the crossing of s and d bands should also apply for the crossing of two d bands, there are a number of observations to support the assignment of the observed structure to emission from surface states of a similar kind. The observations clearly show that the peak in question (Fig. 2) is due to a high density of initial states, as shown also by the field-emission experiments. Band-structure calculations,^{6-8,18,19} which have been shown to give accurate results in the region close to the Fermi surface,¹⁸ predict several regions of high densities of states in the energy range down to 2 eV below the Fermi level. The structure observed in field-emission experiments was assigned in early studies to such a high density of initial states.^{14,15,20} It is not obvious, however, from current band-structure considerations, why the intensity of the structure at -0.9 eV alone should appear so much stronger than other features in the photoemission spectra. In addition, the sensitivity during gas adsorption is different for the various features appearing in the spectra. While adsorbed gases leave the structure at -0.9 and -5 eV relatively unchanged, a drastic effect on the peak assigned to surface states at 0.4 eV is observed, particularly for the case of hydrogen adsorption. It is possible that the $c(2 \times 2)$ superstructure formed by the hydrogen atoms in the β_2 state distorts the d bands at the surface, thereby destroying the basis for the existence of the associated surface states. Indeed a full monolayer of O₂, N₂, or CO is required to suppress emission from the surface states, in agreement with observations by Plummer and Gadzuk.⁹ Finally, it should be noted that measurements performed on photoelectrons emitted normal to the (110) face of tungsten do not show any evidence for surface states. This is in agreement with band-structure theory that

does not predict a gap due to the crossover of bands along the Γ - N direction, which could give rise to surface states.

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Piezo-optical Evidence for Λ Transitions at the 3.4-eV Optical Structure of Silicon

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We report the effects of large uniaxial stresses, which produce splittings and shifts large compared to the spin-orbit interaction, along the [001] and [111] direction on the wavelength-modulated reflectivity spectrum of Si in the region around 3.4 eV. Our results are interpreted in terms of both interband and intraband splittings of the orbital bands and indicate conclusively that the optical structure corresponding to the main peak in reflectivity around 3.4 eV is due to Λ_3 - Λ_1 (or L_3 '- L_1) transitions.

For a number of years there has been considerable controversy concerning the origin of the 3.4-eV optical structure in Si. Both experimental and theoretical evidence have been divided between assignments of the main part of this structure to Δ_5 - Δ_1 transitions (along equivalent [001] axes)¹⁻⁶ or to Λ_3 - Λ_1 transitions (along equivalent [111] axes).⁷⁻¹³ The main experimental evidence for the Δ assignment has been the original chemical-shift data on Ge-Si alloys,¹ dc² and ac³ piezoreflectivity, and, more recently, a study of uniaxial stress on the wavelength-modulated (WLM) spectra.⁵ Doubts concerning the Δ assignment have been raised on the basis of other theoretical⁷⁻¹¹ and experimental work,¹²⁻¹⁶ particularly

with regard to the hydrostatic-pressure coefficient of this structure. Recent electroreflectance experiments on Si¹³ and hydrostatic-pressure investigations of the electroreflectance spectrum of Ge-Si alloys¹² have given strong weight to the Λ assignment. In this Letter we report the effects of uniaxial stresses of up to 23×10^9 dyn cm⁻² along the [111] and [001] directions on the WLM reflectivity spectrum of Si at 77°K, using light polarized parallel (\parallel) and perpendicular (\perp) to the stress axis. These large stresses produce splittings and shifts which are large compared to the spin-orbit interaction (44 meV at $\vec{k}=0$) and hence have enabled us to observe new stress-dependent structures and splittings, which are in-