Electronic Energy Levels of Hydrogen Adsorbed on Tungsten

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The electronic energy levels of hydrogen adsorbed on three low-index planes of tungsten have been studied by a directional photoemission technique for coverages between 0.01 and 1 monolayer. A number of relatively sharp resonance levels are observed, which show half-widths down to 0.5 eV. For the (100) face, a single high-coverage state evolves from multiple low-coverage states, while on the (110) face two states appear to build up sequentially. No pronounced coverage dependence is observed for the (111) face.

Considerable interest has been developed both from a theoretical and an experimental point of view in the adsorption of hydrogen on tungsten. Flash desorption[1-5] and condensation measurements[6-8] have revealed a number of discrete binding states. Low-energy-electron-diffraction (LEED)[9] and reflection high-energy-electron diffraction (RHEED)[10,11] observations show ordered structures that may be correlated to those binding states. Very little is known, however, about the electronic structure of the metal-adsorbate system. Theoretical treatments of adsorption on d-band metals[12-15] show that the electronic states of the free atoms give rise to resonance levels in the local density of states at the surface after adsorption. Such resonance levels have been investigated experimentally by ion-neutralization spectroscopy[16] or by field-emission spectroscopy.[17,18] The latter method has been applied to the hydrogen-tungsten system.[18] Field emission measurements give a good energy resolution, but the available energy range is restricted to less than 2 eV below the Fermi level. Photoelectric emission has been shown to extend this range down to about 10 eV.[19,20]

In the present work a directional photoemission technique,[21] which utilizes a narrow angle of acceptance about the surface normal, is applied to study the adsorption of hydrogen on three low-index crystallographic faces of tungsten. This technique permits the contributions of volume and surface emission in the photoelectric energy distribution spectra[21] to be individually distinguished. The surface photoemission contribution is related to the local density of states at the surface, restricted to small or vanishing components of the k vector parallel to the surface. Changes in the electronic density at the surface due to adsorbed atoms can be detected. Any interpretation of the spectra must take into account the fact that rather than integrating over the surface Brillouin zone, the present technique samples nearly one-dimensional densities restricted to those states about the zone center.

The experimental setup used for the present measurements has been described earlier.[22]

Photoelectrons are generated by focussing a beam of 10.2-eV photons at large angles of incidence onto the sample. An electrostatic 127° analyzer accepts only electrons emitted into a cone of 12° centered at the normal to the single-crystal surface. The energy resolution of the analyzer is 2%. Tungsten single crystals were cut and polished to within 3° of the respective crystallographic plane. A LEED-Auger system was used to check the crystal *in situ* for surface structure and cleanliness. All adsorption measurements were made at room temperature after successive gas exposures.

The heavy curve at the bottom of Fig. 1 shows the energy distribution of photoelectrons emitted normal to the (100) face of clean tungsten at 10.2-eV photon energy. The energy scale refers to initial-state energies relative to the Fermi level.
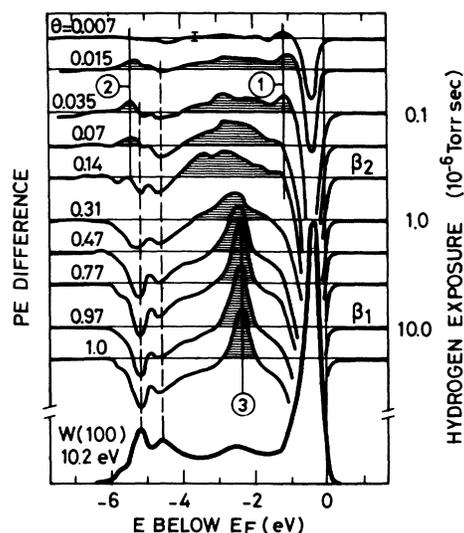

FIG. 1. Photoemission difference spectra for hydrogen adsorption on the (100) face of tungsten. The bottom curve shows the energy distribution spectrum of photoelectrons emitted normal to the clean (100) face. θ gives the fractional coverage corresponding to the difference spectra. Photon energy, 10.2 eV.

The large peak at − 0.4 eV is assigned to emission from surface states,[23] while the two peaks at − 5.2 and − 4.5 eV are due to interband transitions and structure in the surface density of states, respectively.[21] The other curves in Fig. 1 show the difference between the spectrum measured after exposure to hydrogen and the clean substrate spectrum. These curves are shifted vertically such that the exposure may be read from the right-hand scale, increasing from top to bottom. The numbers on the left-hand side give the fractional coverage θ corresponding to each curve. These coverages have been calculated using a sticking coefficient following a $s = s_0(1 - \theta)$ law, which gives a reasonable approximation to the measured sticking coefficient[7] if s_0 is chosen to be 0.2 and a saturation coverage of 1.5×10^{15} atoms/cm^2 is assumed.[24] The saturation coverages for the β_1 and β_2 binding states are also indicated.[1-3]

Positive values of the difference curves are indicative of additional state densities at the surface due to the adsorbate. Those areas are cross-hatched in the figures. Negative values show either suppression of structure in the photoemission energy distribution of clean tungsten or are due to a negative contribution of the adsorbate to the local density of states. As shown by the dashed vertical lines in the figures, all negative structure in the difference spectra lines up with peaks in the spectra of the clean material, indicating that such structure may be related mainly to suppression of peaks in the clean spectra. This is especially drastic for the suppression of the surface-state emission from the (100) face shown in Fig. 1.

At low coverages (top of Fig. 1), two adsorbate levels (marked 1 and 2) are observed at 1.1 and 5.4 eV below the Fermi level. A level similar to 1 has been observed in field emission experiments.[18] The two levels, 1 and 2,[25] appear similar to split virtual levels proposed by Newns.[12] However, in these positions both levels would be filled, so hydrogen would be adsorbed as a negative ion which is unlikely.

For higher exposures, the appearance of these levels is suppressed to some extent by the appearance of a broad double hump about − 3.0 eV as the $c(2 \times 2)$ superstructure characteristic of the β_2 binding state saturates. This change in adsorbate levels might be attributed to increasing interaction between the adsorbed atoms,[26] which leads to the observed superstructure. As the coverage increases further, a single level emerges with a width of only 0.5 eV. This level had also been observed in a photoemission experiment using a polycrystalline tungsten sample.[27] While it cannot be excluded that more structure might exist at energies out of the range of this experiment, the present result suggests that at saturation coverage there is not a co-

existence of hydrogen in the β_1 and β_2 binding states, but rather a complete reorganization of the bonding electrons that leads to the observed narrow adsorbate level. This is consistent with the model proposed by Estrup and Anderson[9] for the atomic arrangement in the β_2 binding state, which suggests that the hydrogen is bonded in equivalent sites rather than partly in molecules and partly in atomic form.[1]

Figure 2 shows the difference spectra for hydrogen adsorbed on a (110) face of tungsten. Again the heavy curve at the bottom shows the energy distribution of electrons emitted normal to the clean surface. All structure in this curve is attributed to surface density-of-states features.[21] The values for the fractional coverage given on the left-hand side of the difference curves have been calculated using $s_0 = 0.07$ and a monolayer coverage of 1.4 $\times 10^{15}$ atoms/cm^2.[7] For low coverages (top curve) there is an indication of two low-coverage levels similar to those observed on the (100) face, the higher level being close to or even above the Fermi level. At coverages that fill the β_2 binding state, an adsorbate resonance level 1 near − 2.8 eV is observed. Another level marked 2, situated at − 4 eV, is observed only for higher coverages and therefore attributed to the β_1 binding state. While in the case of the (100) face the low-coverage adsorbate levels merged into a single one at high coverage, the two resonance levels 1 and 2 on the (110) face are observed to fill sequentially with increasing exposure and appear to coexist at saturation coverage.

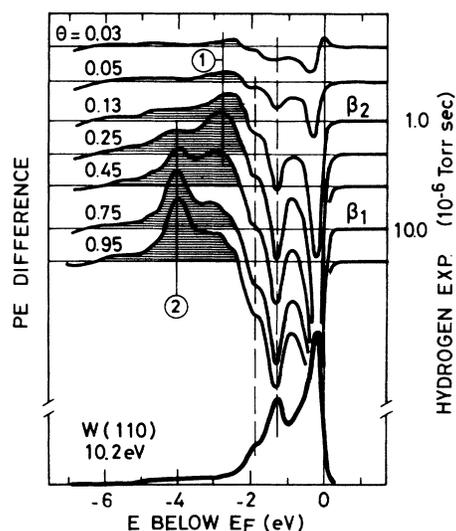The sticking coefficient for hydrogen on the (111) face of tungsten does not follow a simple linear

FIG. 2. Photoemission difference spectra for hydrogen adsorption on the (110) face of tungsten.
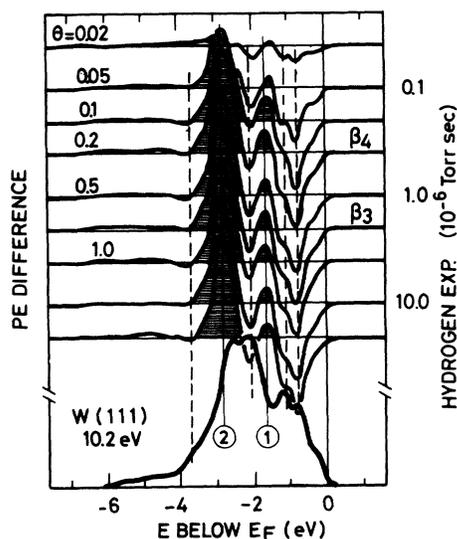
FIG. 3. Photoemission difference spectra for hydrogen adsorption on the (111) face of tungsten.

law.[7] The coverages labeling the difference curves in Fig. 3 for the (111) face therefore have been approximated using a constant sticking coefficient of 0.23. Four discrete binding states are observed for this face by flash desorption,[2,5] two of which survive at 300 °K, namely, β_3 and β_4. Their satur-

ation coverages are indicated in Fig. 3. Analysis of the difference spectra from the (111) face is complicated by the pronounced structure in the energy distribution spectrum from the clean face (bottom curve in Fig. 3). No indication of a low-coverage state is observed as for the other two faces. Two adsorbate levels 1 and 2 are seen at −1.7 and −2.8 eV, but no correlation with the binding states from flash-desorption measurements is obvious. It is even not clear whether structure 1 actually is an adsorbate level or rather a remnant after suppression of peaks from the tungsten photoemission. Structure 2, however, is very strong and has the same width of 0.5 eV as the high-coverage state observed from the (100) face.

A comparison of the difference photoemission spectra for hydrogen adsorption on tungsten shows that strong adsorbate resonance levels are observed on all three faces, with a surprisingly narrow energy width of about 0.5 eV. While sequential filling is observed for two levels on the (110) face, low-coverage states appear to merge into ordered high-coverage states on the (100) face. No pronounced coverage dependence was found for the adatom levels on the (111) face.

We thank M. Adriaens for skilled technical assistance. We are indebted to Dr. R. F. Willis for stimulating discussions and to Professor T. B. Grimley for valuable suggestions.

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