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Chemisorption-Induced Surface Umklapp Processes in Angle-Resolved Synchrotron Photoemission from W(001)†

J. Anderson and G. J. Lapeyre
Montana State University, Bozeman, Montana 59715

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Angle-resolved photoemission, using synchrotron radiation, from the chemisorption system W(001) +H shows a very large doublet of peaks at initial energies −1.3 and −0.6 eV for quarter-monolayer coverage which disappear at higher coverage. The emission lobes are strongly peaked in the ⟨110⟩ azimuths and are attributed to essentially pure bulk W transitions. The electrons are emitted in the new directions through the influence of "extra" surface reciprocal lattice vectors associated with the hydrogen $C(2\times2)$ superstructure.

The appearance of new peaks in photoemission spectra due to chemisorption of atoms or molecules is usually attributed to a modified density of initial states associated with the bonding of the chemisorbed species to the surface.[1] However, chemisorbed layers are known frequently to form ordered overlayers with a corresponding modification in the surface reciprocal lattice. Photoemission theory then implicitly allows the possibility of new emission peaks which we term "kinematic" because they appear solely as a consequence of the new set of reciprocal lattice vectors which may participate in the emission process. As a result, photoemission spectra, particularly angle-resolved spectra from chemisorbed layers, may show new peaks which bear no relation to a possible modified density of initial states. Any interpretation of such data must therefore take into account the possibility that observed structure might have such a purely kinematical origin.

We have observed a rather dramatic manifestation of such an effect in angle-resolved photoemission spectra for the chemisorption system $W(001)+H_2$. A very large doublet of peaks appears at around a quarter monolayer coverage and we present persuasive evidence that this structure is kinematic in character. We identify the doublet as being due to photoemission from essentially bulk W states into new directions as a result of an energy conserving umklapp process involving a new set of surface reciprocal lattice vectors formed by the ordered overlayer of hydrogen atoms.

The tungsten (001) sample was a thin ribbon and standard cleaning procedures were used. The base pressure was $\lesssim 2\times10^{-10}$ Torr. Synchrotron radiation from the storage ring at the University of Wisconsin at Stoughton in the photon energy range 10 eV $\lesssim h\nu \lesssim$ 26 eV was focused on the sample at normal incidence. The resultant s polarization suppresses certain large emission features associated with this system for p polarization.[2] Those features therefore were not present to complicate our observations. With use of a cylindrical mirror analyzer modified with a movable aperture restricting the emission to a 4° cone, angle-resolved energy distribution curves (AREDC's) were measured at azimuthal angle φ and polar angle θ which could be scanned over most of the emission hemisphere.[3] The angle φ was varied by rotating the sample about its surface normal, and we denote that angle by the direction, in the surface, contained in that azimuth, i.e., the ⟨110⟩ azimuth or $\varphi=\langle110\rangle$. The relative hydrogen coverage is denoted by C and saturated coverage, $C=1$, is termed a monolayer of hydrogen atoms. A quarter monolayer is denoted by $H(C/4)$ where values of C were calculated using Madey's[4] results for the sticking co-

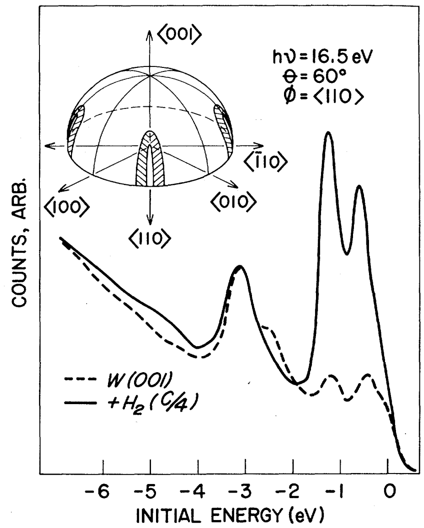

FIG. 1. AREDC's for clean W(001) (dashed line) and W(001) + quarter monolayer hydrogen (solid line). The inset is an emission hemisphere which shows, by shading, the angular properties of the hydrogen-induced structure.

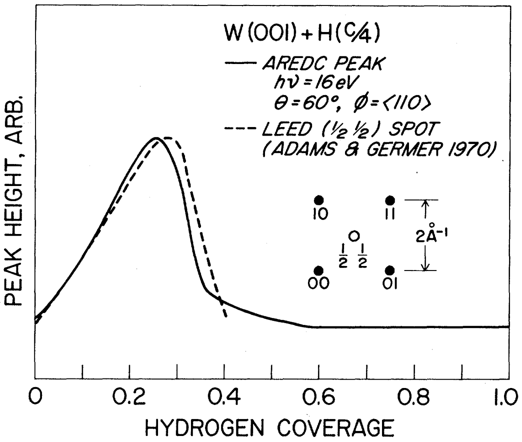

FIG. 2. Amplitude of "new" AREDC doublet peaks versus hydrogen coverage. The inset is a portion of the surface reciprocal lattice showing the "extra" ($\frac{1}{2}$, $\frac{1}{2}$) reciprocal lattice point for W + H($C/4$).

efficient.

The H($C/4$) chemisorption causes only two major ($\gtrsim 15\%$ emission change) structures to appear for the photon energy range studied. *One* is a wide peak at initial energy $E_i = -3.2$ eV (below the Fermi energy) which occurs for $h\nu = 13 \pm 2$ eV. This structure, which appears in the vicinity of $\theta = 30°$, is attributed to a modified state density and will not be discussed further. The other structure, shown in Fig. 1, is a doublet of peaks present for 14 eV $\lesssim h\nu \lesssim$ 24 eV with maximum amplitude near 17 eV. The effect is quite small above 21 eV. The E_i values are about -1.3 and -0.6 eV and are essentially independent of θ and φ. This doublet is attributed to the proposed umklapp process and we have documented its emission properties in some detail. The angular properties of this structure are summarized with the emission hemisphere shown as an inset in Fig. 1. The electrons forming the doublet are emitted in narrow lobes in the four equivalent ⟨110⟩ azimuths, about 15° full width in φ, and over a range of polar angle θ from mid latitudes ($\theta > 52°$) to the horizon. The lobes were not observed for $\theta < 37°$ nor for $\theta = 42.3°$. The lobes bifurcate in the φ angle as the polar angle moves toward the horizon. The polar position at which bifurcation occurs moves nearer the pole (smaller θ) as $h\nu$ or equivalently the final energy increases.

Figure 2 shows the angle-resolved photoemission amplitude as a function of coverage which indicates that the structure is associated with the quarter-monolayer phenomena found in low-energy electron diffraction (LEED) studies.[5] The amplitude increases almost linearly to a maximum at $C = 0.25$ followed by a rapid decrease to $C \approx 0.35$ and then a slower decrease to $C \approx 0.5$ after which the doublet structure is gone. LEED observations[5] have shown that hydrogen adsorption near $C = \frac{1}{4}$ produces a centered (2×2) surface structure instead of the primitive (1×1) structure for clean W(100) and for saturated H chemisorption: The unit LEED pattern exhibits an "extra" ($\frac{1}{2}$, $\frac{1}{2}$) or center spot. The inset in Fig. 2 shows a portion of the surface reciprocal lattice and the location of the "extra" ($\frac{1}{2}$, $\frac{1}{2}$) point associated with the C(2×2) structure. The corresponding reciprocal lattice vector, which we call $\vec{G}_N$, has a length 1.41 Å^{-1}.

In interpreting the photoemission properties of this system we consider a plane-wave expansion of the wave functions for the system[6]:

$$\psi_{\vec{k}_\parallel}(\vec{r}) \propto \sum_{\vec{G}_\parallel} C_{\vec{G}_\parallel \vec{k}_\parallel}(z) \exp[i(\vec{k}_\parallel + \vec{G}_\parallel)\cdot\vec{r}],$$

where z is the distance into the crystal, and $\vec{G}_\parallel$ and $\vec{k}_\parallel$ are the components, parallel to the surface, of the reciprocal lattice vector $\vec{G}$ and wave vector $\vec{k}$. For the H($C/4$) system the sum must include the terms resulting from the new reciprocal lattice vector $\vec{G}_N$. Since the parallel component of momentum is conserved in the process of emission into the vacuum,[7] inclusion of $\vec{G}_N$

gives rise to the possibility of observing photocurrent in the azimuth containing $\vec{k}_\parallel + \vec{G}_N$.[7] We propose an interpretation in which the hydrogen-induced structure under consideration is attributed to transitions between states of predominantly bulk W character (near Γ) along the Δ line which has $\vec{k}_\parallel = 0$ in the reduced Brillouin zone, but emitted in new directions by an umklapp process. The new participating reciprocal lattice vector is $\vec{G}_N$ so that the electrons are emitted in the ⟨110⟩ azimuth. The process can be equivalently pictured as the extra reciprocal lattice vector allowing a new class of $\vec{k}$-conserving direct transitions in the appropriate reduced-zone scheme *or* as optical excitation followed by final-state scattering where the new lattice vectors have to be included.

Stated in electron diffraction terms, the phenomenon is the same umklapp process that gives rise to the "extra" LEED center spots indexed as $(\frac{1}{2},\frac{1}{2})$ in the $C(2\times 2)$ pattern. One would therefore expect similar behavior in the intensity of LEED and photoemission peaks as a function of hydrogen coverage. The LEED $(\frac{1}{2},\frac{1}{2})$ spot intensity data shown in Fig. 2 were taken from the data of Adams and Germer.[5] We have converted those data to intensity versus coverage, normalizing the maximum amplitude to our data and taking account of the background under the photoemission peaks. The striking similarity of the two curves supports the interpretation.

As further evidence, Fig. 3 shows a set of normal-emission AREDC's (initial $\vec{k}_\parallel = 0$) for clean W(001). The prominent doublet shown in these curves is attributed to flat d-like bulk band-structure states just below E_F, along the Δ symmetry line in the Brillouin zone (the ⟨001⟩ symmetry axis).[8] Plotted with the clean normal spectra in Fig. 3 are the differences between the clean and corresponding chemisorbed AREDC's like those shown in Fig. 1. The *difference* curves manifest only the effects of $H(C/4)$. The following points of similarity in the two sets of spectra are evident: (1) Both are doublets; (2) even including the small $h\nu$ dispersion (~0.5 eV) of the 1.3-eV peak, the peak positions of the doublets agree curve for curve to about 0.1 eV; and (3) both exhibit the inversion of the relative peak amplitudes with increasing $h\nu$, which occurs around 16 eV. Thus the observed energetics are consistent with those implicit in the proposed model.

The wave-vector properties of the $H(C/4)$ doublet are also consistent with those required by the model. First, the direction is properly in the ⟨110⟩ azimuth as noted earlier. Secondly, since the parallel momentum is conserved in electron emission, its value can be determined from the kinetic energy, E_k, of the emitted electron: $p_\parallel = \hbar^{-1}(2mE_k)^{1/2}\sin\theta$. The umklapp model implies $p_\parallel = |\vec{G}_N| = 1.41\ \text{Å}^{-1}$ only for excitation of states on the Δ line for which $k_\parallel = 0$. Undoubtedly states in the neighborhood of the Δ line can be excited, too, and we believe that this accounts for our observation that enhancement can be detected over the range $1.2\ \text{Å}^{-1} \lesssim p_\parallel \lesssim 2.0\ \text{Å}^{-1}$. However, the doublets are strong only for $p_\parallel \gtrsim 1.4\ \text{Å}^{-1}$. The bifurcation may be due to excitation of states displaced from, but symmetrically disposed about, the Δ line. If the latter suggestion is correct, the lobes should bifurcate for $p_\parallel \neq 1.41\ \text{Å}^{-1}$. We note that for various combinations of θ and $h\nu$, the bifurcation occurs only for $p_\parallel \gtrsim 1.5\ \text{Å}^{-1}$.

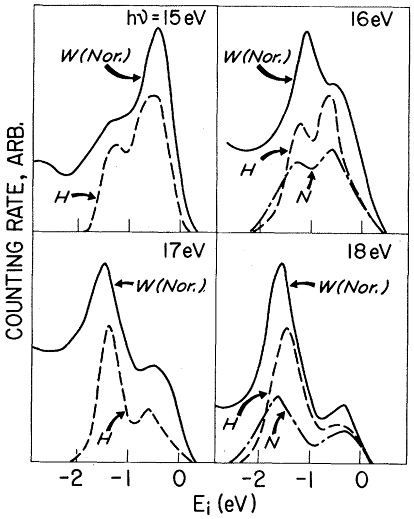

FIG. 3. Comparison of clean W normal-emission AREDC's (solid lines) to $W+H(C/4)$ difference curves (dashed lines) ($\theta = 75°$ for $h\nu = 15$ eV; $\theta = 60°$ for $h\nu = 16$, 17, 18 eV). Nitrogen difference curves are dot-dashed lines. All curves are normalized for convenient presentation.

It would appear from the above discussion that, in principle, such effects must necessarily be present to some degree for ordered overlayer systems and should be taken into account in analyzing angle-resolved photoemission data. This would also hold for reconstructed clean surfaces, and Traum, Rowe, and Smith[9] have suggested that such an effect might be present in their photoemission data for Si(111). Even in the case where the surface periodicity is not altered, the chemisorbed atoms might modify the photoemission current through their influence on the scattering amplitudes involved in the umklapp processes. As one test case we have examined saturated nitrogen on W(001) which also has $C(2\times 2)$ LEED structure.[10] The results showed a large chemisorption-induced doublet with properties very similar to those presented here for $\mathrm{H}(C/4)$, as the model predicted. A pair of nitrogen difference curves are shown in Fig. 3. The behavior of intensity versus coverage, C, merits mention. Nitrogen is known to adsorb in a rather less ordered manner than hydrogen[10] and we had therefore expected to observe a lower intensity increase[10] than the nearly linear behavior of hydrogen shown in Fig. 2. The intensity was, indeed, found to be concave upwards with zero slope at $C=0$ and fairly well represented by a C^2 dependence over much of the coverage range. We regard the nitrogen observations as strong corroboration for our model.

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Plasma Radiation from Tunnel Junctions[*]

Tien-Lai Hwang, S. E. Schwarz, and R. K. Jain[†]
Department of Electrical Engineering and Computer Sciences and the Electronics Research Laboratory,
University of California at Berkeley, Berkeley, California 94720

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Electromagnetic radiation with a spectrum sharply concentrated near the bulk plasma frequency of silver has been observed in emission from Al-$\mathrm{Al_2O_3}$-Ag planar tunnel junctions.

It is well known that metal foils irradiated with beams of energetic electrons can emit electromagnetic radiation, with a spectrum concentrated near the bulk plasma frequency.[1-3] In this Letter we report observation of similar radiation excited by low-energy electrons in planar aluminum-aluminum-oxide-silver tunnel junctions. Although the fundamental mechanisms of photon emission appear similar to those in high-energy experiments, we are now observing them in the "quantum" regime where electron energy is approximately equal to $\hbar\omega_p$. Furthermore, tunnel structures are rather different experimentally, and thus offer new opportunities for studies of plasma oscillations in metals.

The tunnel junctions were made by evaporating, on a glass substrate, an aluminum strip of approximately 750 Å thickness. The aluminum was oxidized by a plasma oxidation technique and a perpendicular strip of silver (thickness approximately 175 Å) was then evaporated across it. The junction area was 1.8×10^{-4} cm^2, and from capacitance measurements we estimate the oxide thickness to be 30 Å. At room temperature the