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# Unoccupied surface states on W(001) and Mo(001) by inverse photoemission

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The W(001) and Mo(001) surfaces are investigated by inverse photoemission. At $\bar{\Gamma}$ we observe an unoccupied surface state just above the Fermi level. The angular dependence and chemisorption behavior identify it as a $d_{z^2}$ surface state similar to one observed and calculated just below $E_F$. For W(001) a second state is seen near $\bar{M}$ at 1.4 eV above $E_F$ and assigned to a $\bar{\Sigma}_2$ back-bonding state. The implications of our data on the driving mechanism for the surface reconstruction are discussed using all-electron self-consistent local-density calculations.

Considerable experimental and theoretical efforts have been devoted to the study of the (001) surfaces of tungsten and molybdenum, especially to the electronic surface states located near the Fermi level.[1-16] These materials were used in the field emission and photoemission studies that pioneered the study of surface states.[1] The choice of W(001) and Mo(001) is in part motivated by the observation of surface reconstruction on these surfaces at low temperature [$\sqrt{2}\times\sqrt{2}R45°=c(2\times2)$ for W(001)[2] and a similar but incommensurate structure for Mo(001)[3]]. They represent relatively simple model systems for understanding the driving force for surface reconstruction on metals. Several mechanisms have been proposed[8] [e.g., a charge-density wave (CDW) at $\mathbf{k}_\parallel=\bar{\Gamma}\bar{M}$, local bonding by a back-bonding state] all involving electronic surface states near the Fermi level. So far, only the occupied half of these states has been measured. Inverse photoemission makes the unoccupied states accessible to experiment.

Our results for W(001) and Mo(001) exhibit an unoccupied surface state near $\bar{\Gamma}$ which is assigned to a $d_{z^2}$-type resonance between surface and bulk states and a second state near $\bar{M}$ which likely corresponds to a $\bar{\Sigma}_2$ back-bonding state. No strong unoccupied surface state is found near $\frac{1}{2}\bar{\Gamma}\bar{M}$ of the $1\times1$ Brillouin zone as required in CDW models and predicted by local-density theory. The observation of a $d_{z^2}$ surface state on W and Mo has implications in several areas. In scanning tunneling microscopy and spectroscopy the probe-tip material is usually W. In order to describe the tunneling process quantitatively it is essential to know the density of surface states with wave functions extending out from the surface. Their energy position is crucial for interpreting data in the spectroscopy mode. New territory is charted in the area of surface states. To our knowledge no $d$-like unoccupied surface states ("Tamm" states) have been observed previously,[9] only the free-electron-like image-potential states and $s,p$ states ("Shockley" states). The localized $d$ states play an important role in transition-metal surface chemistry and surface magnetism.

The experiment was performed with a state-of-the-art high-resolution inverse photoemission spectrometer[17] with simultaneous detection of photons between 8 and 30 eV. The spectrometer with a base pressure of some $10^{-11}$ Torr is connected via an interlock to a separate sample-preparation chamber (base pressure $<1\times10^{-10}$ Torr). The samples were cleaned by repetitive oxidization and heat treatment as described elsewhere.[10] All spectra were taken at room temperature.

Figure 1(a) shows inverse photoemission spectra from W(001) recorded at normal electron incidence (i.e., for vanishing momentum parallel to the surface, $k_\parallel=0$). Each spectrum corresponds to the energy distribution of the emitted photons for a given energy $E_i$ of the incident electron beam with high photon energies toward the left. The momentum perpendicular to the surface ($k_\perp$) is changed by varying the energy $E_i$. The peak observed 0.25 eV above the Fermi level shows no $k_\perp$ dispersion and is highly sensitive to contamination [Figs. 1(b) and 1(c)]. Therefore it is interpreted as due to a surface state. A small peak at 3.9 eV, which is also contamination sensitive and does not disperse with $k_\perp$, is due to an image-potential surface state that is located about 0.7 eV below the vacuum level, well within the range of binding energies observed on other metals.[18] It is interesting to observe that such image states do occur on bcc metals since previous observations were made on fcc metals. A broad structure around 3 eV above $E_F$ is insensitive to contamination and changes strongly with $E_i$ which classifies it as a bulk interband transition. We tentatively assign it to a saddle point in the $\Delta_1$ bulk band from $\Gamma_{12}$ to $H_{15}$ (Fig. 2). The spectra from Mo(001) exhibit surface and bulk states analogous to those for W(001) as shown in Figs. 1(b) and 1(c).

In order to interpret the surface states we start with self-consistent slab calculations for an unreconstructed $1\times1$ surface[11] and for the reconstructed surface (Fig. 2, full and dashed lines, respectively). A wealth of surface states has been reported both experimentally and theoretically. However, if one considers only states with a charge

 

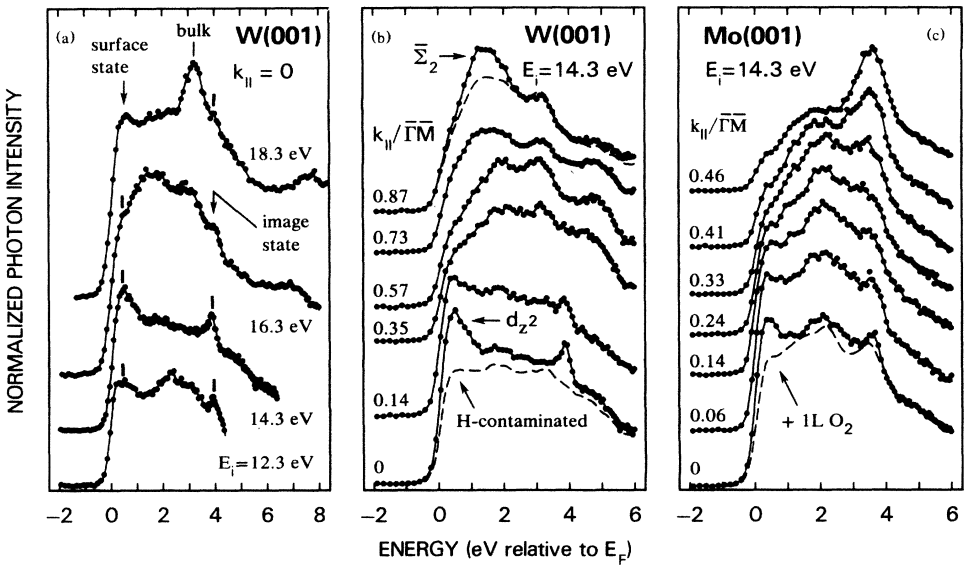


FIG. 1. Inverse photoemission spectra from W(001) and Mo(001). (a) Energy dependence at $k_{\parallel}=0$. Two-dimensional states such as the intrinsic surface state near $E_F$ and the image potential state at $E_F+3.9$ eV are characterized by the absence of $E$ vs $k_{\perp}$ band dispersion, which is mapped by tuning the incident electron energy $E_i$. (b) and (c) Angular dependence along the [110] direction ($\bar{\Gamma}\bar{\Sigma}\bar{M}$ in the 1×1 surface Brillouin zone). The $d_{z^2}$ surface state at $\bar{\Gamma}$ becomes weaker with increasing $k_{\parallel}$. At $\frac{1}{2}\bar{\Gamma}\bar{M}$ there is a minimum in the density of states at $E_F$. The strong peak near $\bar{M}$ at $E_F+1.4$ eV is assigned to the $\bar{\Sigma}_2$ back-bonding state.

density concentrated in the outermost layer, the picture is dramatically simplified. Using the calculation of Ohnishi, Freeman, and Wimmer[11] one finds two such states along the high symmetry line $\bar{\Gamma}\bar{\Sigma}\bar{M}$, i.e., a $d_{z^2}$ state just below $E_F$ near $\bar{\Gamma}$ (labeled HL SS in Ref. 11) and an odd $\bar{\Sigma}_2$ state along the $\bar{\Sigma}$ line (*A*,*B* in Ref. 11). All other states extend over several layers, including an even $\bar{\Sigma}_1$ state (*E*,*F* in Ref. 11) near $E_F$, a lower surface state at $\bar{\Gamma}$ (LL SS), and unoccupied states that lie near the state observed in inverse photoemission (*G*,*H* in Ref. 11). The localized $d_{z^2}$ and the $\bar{\Sigma}_2$ state have both been observed with photoemission.[12–14]

The $\bar{\Sigma}_2$ and $\bar{\Sigma}_1$ states, associated with the surface reconstruction of W(001),[8,11,13,15] have an orbital character that bonds the surface atoms to other surface atoms and to sub-

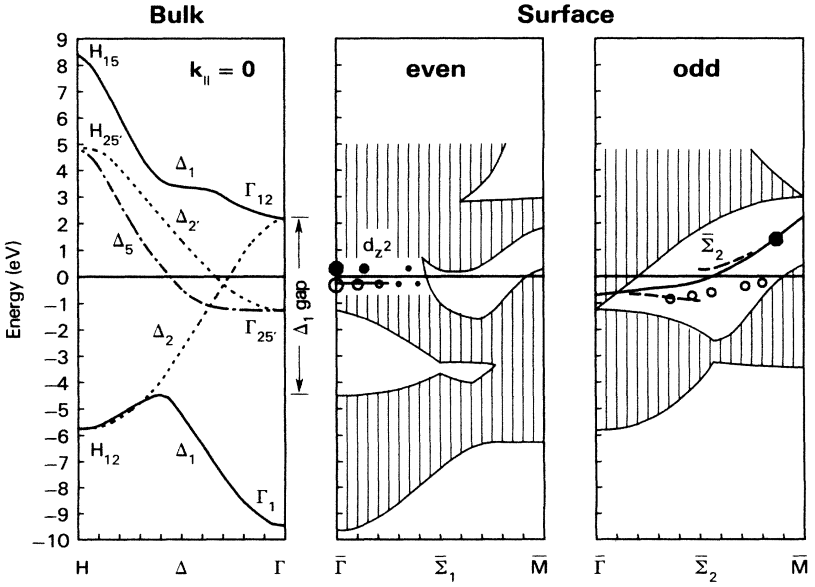


FIG. 2. Bulk and surface band structure of W(001)1×1 (bulk bands after Refs. 4 and 5, and surface bands after Ref. 11). Only the states with strongest surface localization (Ref. 11) are shown, i.e., a $\bar{\Sigma}_1$ state near $\bar{\Gamma}$ with dangling bond character ($d_{z^2}$) and a $\bar{\Sigma}_2$ state with a back-bond character ($d_{xz}$). The dashed surface bonds (shown unfolded) are calculated self-consistently for the $c(2\times2)$ reconstruction which introduces a new zone boundary at $\frac{1}{2}\bar{\Gamma}\bar{M}$. Inverse photoemission results are shown as dots, photoemission (Ref. 14) results as open circles.

surface atoms. Half of these bonds are shortened (and strengthened) in the reconstruction model of Debe and King[2] where the surface atom moves along the [110] direction. The $\bar{\Sigma}_2$ band has been proposed as supporting a CDW model for the surface reconstruction because it is calculated to intersect $E_F$ near $\frac{1}{2}\bar{\Gamma}\bar{M}$ in the $1\times1$ structure. Our calculation shows that the reconstruction opens a gap in the $\bar{\Sigma}_2$ band at $\frac{1}{2}\bar{\Gamma}\bar{M}$ (see Fig. 2, dashed line) and that this gapping occurs over a large part of the surface Brillouin zone in both the [110] and [1$\bar{1}$0] directions. It appears that a local-bonding enhancement arising from the unstable high density of states at $E_F$ in the $1\times1$ structure is a more appropriate mechanism for the reconstruction. [Analysis of the symmetry of the wave-function characters of the $\bar{\Sigma}_1$ and $\bar{\Sigma}_2$ states also demonstrates that the zigzag chain displacement of the surface atoms can be explained in terms of the coupling of the $d_{x^2-y^2}(\bar{\Sigma}_2)$ to the $d_{xy}(\bar{\Sigma}_1)$ orbitals.[19]] In our inverse photoemission experiments at room temperature, however, we do not observe any state at $\frac{1}{2}\bar{\Gamma}\bar{M}$ that could represent the expected unoccupied upper state. A candidate for the $\bar{\Sigma}_2$ state is not observed until $0.8\bar{\Gamma}\bar{M}$, where a strong peak appears at $E_F+1.4$ eV [see Fig. 1(b)]. It is located in a bulk band gap of the $1\times1$ structure and, therefore, has to be either a surface state or a bulk state at $\bar{\Gamma}$ seen via surface umklapp. The lack of an observed unoccupied surface state near $\frac{1}{2}\bar{\Gamma}\bar{M}$ is not understood at present. The data indicate a reduced splitting and/or a lowering of the $\bar{\Sigma}_2$ band by up to 0.5 eV.[20] One has to keep in mind that at room temperature the surface reconstruction seen by low-energy electron diffraction has almost disappeared, either due to a very small size of the reconstructed areas, or due to a continuous phase transition to an ordered $1\times1$ structure.[2]

The $d_{z^2}$ state calculated at $E_F$-0.3 eV has dangling-bond character and is well known as an occupied state.[1,10,16] The unoccupied surface state seen near $\bar{\Gamma}$ is assigned to a surface resonance derived from this $d_{z^2}$ state. This surface state broadens by mixing with bulk states to about 1 eV full width at half maximum and extends from its center below $E_F$ significantly above $E_F$. We base our assignment on striking analogies between inverse photoemission and photoemission data when the chemisorption behavior is compared. For W(001) we find the unoccupied surface state to be extremely sensitive to residual gas (mostly hydrogen). It is quenched by exposures less than 1 L (1 L $=10^{-6}$ Torr sec). For Mo(001) much more $H_2$ (about 80 L) but only 1 L $O_2$ is needed to quench the state. The angular dependence [Figs. 1(b) and 1(c)] is characterized by a strongly decreasing intensity away from $\bar{\Gamma}$. A similar intensity decrease is observed with photoemission but has been attributed to a band dispersion through the Fermi level.[13,14] Such a dispersion is ruled out by our inverse photoemission results which lack a band appearing above $E_F$. Instead one can explain the intensity decrease by increasing hybridization with bulk states. The $\bar{\Gamma}_1$ surface state is located near the middle of a symmetry gap of $\Delta_1$ bulk states (see Fig. 2) which exists only at $\bar{\Gamma}$. Away from the $\bar{\Gamma}$ the bulk states connected with the $\Delta_5$ band mix with the surface state and quench it. Likewise, a small amount of disorder, e.g., induced by chemisorbed atoms, causes momentum transfer and mixes bulk states with $\mathbf{k}_\parallel\neq0$ to the surface state. This explains why the surface state on W(001) is extremely sensitive to surface cleanliness. Note that a strikingly similar intensity falloff and adsorbate sensitivity have been seen for a $\Lambda_1$ surface state on Ni(111),[21] which is also located in a symmetry gap that only exists at $k_\parallel=0$. For reconstructed W(001) and Mo(001) one expects additional momentum transfer from boundaries between different domain orientations. Finally, spin-orbit interaction[4] also mixes bulk states of $\Delta_1$ and $\Delta_5$ symmetry. Although spin-orbit effects should be much stronger for W than for Mo, no significant difference is observed in our experiment.

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