H and the W(001) Surface Reconstructions: Local Bonding to Surface States

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The structural properties of the W(001)$p(1\times1)$-2H system are predicted by use of all-electron total-energy calculations. Both the vibrational frequency (133 meV) and the work-function change (0.95 eV) are in excellent agreement with experiment at the calculated equilibrium H-W interlayer spacing of 1.12 Å. A proposed electronic driving mechanism, which includes local bonding effects and depends on the character of the $\bar{\Sigma}_2$ surface-state wave functions, explains the various observed reconstructions of the clean-W(001) and H/W(001) systems, including symmetries and coverage dependence.

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The W(001) surface is one of the best studied in surface science because of the wealth of different physical phenomena that it exhibits.[1] Of particular interest has been the temperature-induced phase transition of the clean surface and the unusual phase diagram versus hydrogen coverage. By now it is rather well established that the so-called Debe-King model[2] [cf. Fig. 1(a)] describes the low-temperature phase of the clean surface, but there is still controversy concerning the origin of the reconstruction: The phase transition from the high-temperature $p(1\times1)$ to the low-temperature $c(2\times2)$ $p2mg$ structure was first explained[3,4] in terms of Fermi-surface nesting in which states of $\pm k$ near the new zone boundary mix, but photoemission experiments[5] have demonstrated that the surface-state coupling is too small to drive the transition. On the other hand, frozen-phonon total-energy local-density calculations[6] have shown that the Debe-King model is energetically favored and that upon reconstruction there is a substantial splitting and decrease of the density of states at the Fermi level. These investigations, however, did not determine the underlying mechanism which drives the transition. In contrast to the clean surface, hydrogen (which adsorbs in the bridge site at all coverages) dramatically changes the $c(2\times2)$ $p2mg$ reconstruction: Up to about half a monolayer coverage ($\theta=0.5$), the surface is again reconstructed but into a $c(2\times2)$ $c2mm$ structure [Fig. 1(b)]; at saturation coverage ($\theta=2$), the surface returns to the $p(1\times1)$ structure.[7,8]

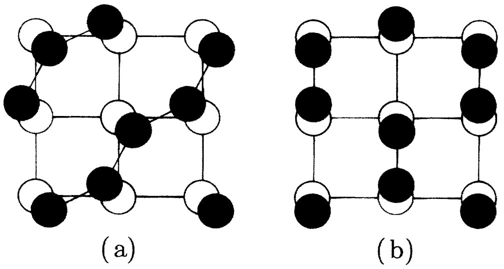

FIG. 1. Schematic of the (a) $p2mg$ and (b) $c2mm$ W(001) surface reconstructions. Filled circles show the position of the displaced atoms upon reconstruction.

A number of authors have calculated various aspects of the electronic structure of the clean[9-11] and hydrogen-covered[12] surfaces, with particular emphasis on the location of the surface states. In this paper we consider theoretically the equilibrium properties of H on the W(001) surface and the origin of the phase transitions observed for both the clean surface and the hydrogen-saturated W(001)$p(1\times1)$-2H surface. We make predictions for (i) the H position above the W surface (which favors the LEED,[13] rather than the high-resolution electron-energy-loss spectroscopy[14] value) and (ii) the vibrational frequency of the symmetric stretch mode and the work-function change on hydrogen adsorption (both in excellent agreement with experiment). More importantly, from comparisons of the clean and hydrogen-covered surfaces, we are able to identify the mechanism driving the surface reconstruction. On this basis, we propose a model that naturally accounts for the various reconstructions, including the symmetry of the clean surface and the symmetry switching of the reconstruction with the adsorption of hydrogen.

The surfaces were modeled by a seven-layer ideal W(001) film with an additional layer on each side consisting of two bridge-bonded atoms per surface unit cell. To simulate both systems, the nuclear charge inside these atomic spheres is either zero (clean surface) or unity (H covered). The calculations were done within the local-density framework using the full-potential linearized augmented plane-wave method.[15,16] In this method, the scalar relativistic single-particle equations for the valence states are solved self-consistently without shape approximations to either the density or the potential. The relativistic core is recalculated in each iteration. The troublesome semicore $5p$ electrons (which have ~0.1 electron per W atom outside touching muffin-tin spheres) are treated as bands in a separate energy window. This treatment allows the $5p$ electrons self-consistently to adjust (and contribute) to the nonspherical surface potential. (The effect of correctly treating these states as bands causes small but noticeable changes compared to test calculations in which the density due to these electrons was either arbitrarily frozen or constrained to be a sum of overlapping single-site densities. Similar tests for the $4f$ levels showed that these states could be treated accurately as core states in the usual way.)

Since previous calculations using the full-potential linearized augmented plane-wave method for the clean surface have given detailed information about the surface states[10,11] and the energetics of interlayer relaxation[17] and reconstruction,[6] we do not discuss these aspects in detail. The clean W(001) surface has a calculated work function, ϕ, of 4.63 eV determined by use of the Wigner[18] exchange-correlation potential—in excellent agreement with the experimental value of 4.62 eV.[19] Changing the functional form of the exchange-correlation changes this value by ~0.1 eV. (For example, using the Ceperly-Adler Monte Carlo results as parametrized by Vosko, Wilk, and Nusair[20] yields $\phi = 4.53$ eV, still in good agreement with experiment.)

The equilibrium properties of the bridge-bonded hydrogen layer were determined from a set of self-consistent calculations in which the interlayer separation between the H layer and the W surface, $d_{\text{W-H}}$, was varied. From the total energy,[16] we find that $d_{\text{W-H}} = 1.12 \pm 0.01$ Å with a symmetric-stretch-mode vibrational frequency of 133 ± 4 meV. Recently, experimental determinations of $d_{\text{W-H}}$ have been reported, ranging from 1.17 ± 0.04 Å as determined by LEED[13] to 1.74 Å as inferred from high-resolution electron-energy-loss spectroscopy measurements.[14] Our results strongly support the shorter distance: The calculated value of the vibrational frequency is in excellent agreement with the experimental value of 130 meV,[21] as is the calculated work-function change, $\Delta\phi = 0.95$ eV, compared to experiment,[22] $\Delta\phi = 0.90$ eV (recent experimental references[23] now also quote a value of 0.95 eV), demonstrating that a value of $d_{\text{W-H}} \simeq 1.12$ Å is consistent with experiments.

On the clean surface, there is a well known $\bar{\Sigma}_2$ band of surface states that crosses the Fermi level approximately midway to the edge of the zone. The effect of H is to remove this band from the gap,[24] and to cause various other changes in the surface-state spectrum. We propose that the reconstructions of both the clean and H-covered surfaces are driven by this band of surface states, but in contrast to previous proposals,[3,4] we suggest that the shape of the wave functions is the essential aspect of the problem. The actual physical parameters and interactions are important to an understanding of these phase transitions since the W(001) reconstruction belongs to a class of models[25] which exhibit nonuniversal behavior. The *microscopic* picture of the reconstructions presented here thus provides a basis for effective Hamiltonian treatments.[26] Furthermore, we emphasize that experiments[5] and calculations[6] do not explain why the reconstruction occurs, but rather give the properties of the reconstructed phase, e.g., changes in density of states. Our model of the driving mechanism is consistent with these results.

The essential physics is contained in Fig. 2 which shows $|\psi|^2$ plotted in a plane parallel to the surface at a height appropriate to the H overlayer for the W(001) (odd) $\bar{\Sigma}_2$ surface state at a point in k halfway towards the zone boundary. Plots for other points along the $\bar{\Sigma}$ line for this surface-state band are remarkably similar, although the magnitudes of the peaks in this plane do vary. The similarity between Fig. 2 and the Debe-King model [Fig. 1(a)] is obvious and leads to a simple explanation of the driving mechanism for the phase transitions. Our picture is that in a given phase region, the wave function is preferentially increased in magnitude resulting in an increased charge density. Putting aside for the moment how this increase comes about, it is easy to see that this change in charge density

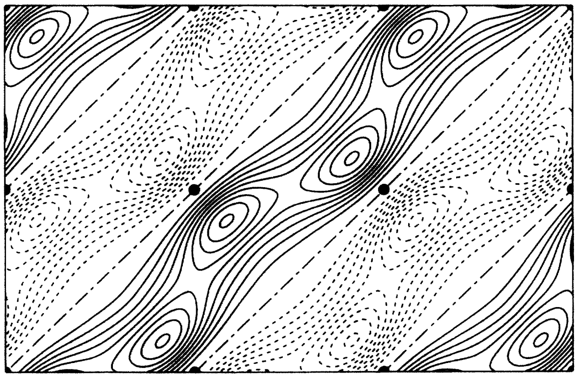

FIG. 2. $|\psi|^2$ of the W(001) $\bar{\Sigma}_2$ surface state midway to the Brillouin-zone edge in a plane parallel to the surface and at a height appropriate to the H layer. The dash-dotted lines mark nodes, filled circles mark the positions of the $p(1\times1)$ surface W atoms, and the contours are in units of 10^{-4} a.u. (Contours for regions with negative relative phase are dashed.)

results in an electrostatic attraction of the W atoms towards the peaks in the density. (This electrostatic force is a simple consequence of the electrostatic form of the Hellmann-Feynman theorem.[27]) Since the driving force is electrostatic in nature, the required charge imbalance can be quite small. (Once the transition occurs, so will changes in the density of states; however, these changes by themselves cannot account for the transition.[5]) The temperature dependence of the phase transition is due to entropy considerations and/or temperature-dependent variations in the charge imbalance.

At this point we must address whether this model is consistent with symmetry considerations and whether the proposed preferential increase in charge density is reasonable. The simplest way to increase one phase of an odd wave function preferentially over the other is to add in the corresponding even state. On the W(001) surface, a band of $\bar{\Sigma}_1$ surface states exists by in energy with the correct orbital character. Furthermore, the reduced $p2mg$ symmetry of the reconstruction (a glide rather than a mirror plane) allows these two states to mix. (The perturbation due to the reconstruction obviously has both an even and an odd part with respect to the mirror plane. Hence, both perturbation theory and more detailed calculations show the charge-density changes required by our model.) Finally, if one includes spin-orbit effects, the proper relativistic wave functions of the ideal $p(1\times1)$ structure will already be mixtures of the even and odd states.

A consequence of this picture is that the exact position where the $\bar{\Sigma}_2$ band crosses the Fermi level is not of special importance in determining the resulting structure. Rather the doubling of the unit cell can be argued differently: The two $\bar{\Sigma}$ directions in the $p(1\times1)$ structure imply that there should be two domain orientations. Considering the phase transition as a soft phonon of a single k vector[28] implies that the photon must be doubly degenerate. The only points in the $p(1\times1)$ surface Brillouin zone that have doubly degenerate irreducible representations are $\bar{\Gamma}$ and $\bar{M}$; however, since $\bar{\Gamma}$ phonons do not change the translational symmetry (unit cell), the soft phonons must belong to the $\bar{M}_5$ irreducible representation.

The effect of H on the reconstruction likewise can be understood from Fig. 2. (The H adsorption site is determined by the overall energetics, ~3.2 eV per H atom, and not by the $\bar{\Sigma}_2$ state alone.) The calculations show that the H interacts strongly with the $\bar{\Sigma}_2$ surface states. Consider a hydrogen sitting on a bridge site where the phase of the $\bar{\Sigma}_2$ surface state is positive. The effect on the wave function will be to pull the peaks toward the H atom—in a local bonding picture, one is forming bonds between the H and W atoms. This is shown in Fig. 3, where we present the valence charge density of the $p(1\times1)$-2H surface in the plane of the H atoms, and the corresponding charge rearrangement due to H chemisorption. The significant charge rearrangements, in particular the increase between the H and W atoms, demonstrates the formation of strong covalent H—W bonds. The change in electron density will, as for the clean surface, cause an electrostatic attraction of the W atoms toward the resulting peaks of $|\psi|^2$ (cf. Fig. 3), i.e., towards the H sites. The band nature (translational symmetry) of the wave functions will cause the H-induced distortion to extend beyond the near-neighbor W atoms. Hence, even for small H concentrations, an ordered $c(2\times2)$ W reconstruction with space-group symmetry $c2mm$ is expected. As for the clean reconstruction, we again expect two orientations of domains.

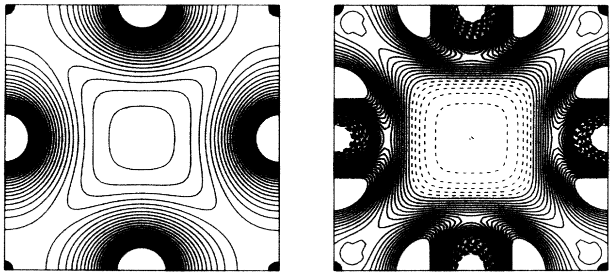

FIG. 3. (a) Charge density for the W(001)$p(1\times1)$-2H surface in the plane of the H atoms. The surface W atoms are at the corners of the square (filled circles) and the H are in the bridge sites. Contour spacing is 10^{-3} a.u. (b) Difference density between the H-covered surface and the sum of the clean surface plus atomic H in units of 10^{-4} a.u. Negative contours are dotted.

For H coverages above $\theta = 0.5$, all of one type of H sites (i.e., positive-phase short-bridge sites) are filled and then the extra H must go onto other bridge sites. At these higher H concentrations there are no simple patterns in our model until one reaches saturation coverage of $\theta = 2$, at which point all bridge sites are occupied, and one expects a $p(1\times1)$ structure again. Hence, we would expect a crossover from the $c(2\times2)$ $c2mm$ reconstruction to either an incommensurate or a disordered phase at $\theta = 0.5$ based on filling of the bridge sites in the proposed order. In reality of course, temperature-induced surface mobility of the H atoms and the deposition process itself will cause other bridge sites to be occupied, resulting in competing distortions. This distribution of distortion destroys the long-range translational symmetry necessary for LEED and causes the transition to shift to lower coverages ($\theta < 0.5$) for higher temperatures. These results are consistent with the phase diagram reported by Barker and Estrup.[8]

In summary, we have carried out a series of self-consistent local-density calculations of H chemisorbed on the W(001) surface. Our predicted values for the vibrational frequency and work-function change are in excellent agreement with experiment, supporting a calculated H-W interlayer spacing of 1.12 Å, in good agreement with LEED.[13] The H is found to interact strongly with the $\bar{\Sigma}_2$ band of surface states. From these results we propose that the reconstructions observed for the H/W(001) system are electronically driven by local bonding effects of the surface-state bands. Our model is able, in a simple way, to account for the clean reconstruction and the symmetry switching with the addition of H. In addition, we do not require that the surface-state band intersect the Fermi level at any particular place, but rather the whole band is able to contribute to the electrostatic forces that drive the surface reconstruction. Finally, we emphasize that the symmetries of the various phases are direct consequences of our model—this is apparently the first model to predict correctly the various phase transitions *and* at the same time provide a microscopic mechanism for the different H/W(001) reconstructions.

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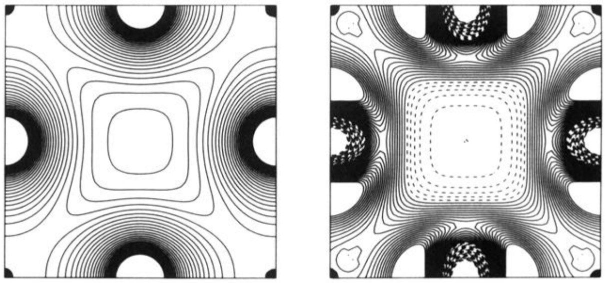

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