PHYSICAL REVIEW B VOLUME 37, NUMBER 14 15 MAY 1988-I

Electronic contributions to the hydrogen-induced reconstruction of W(110)

R. H. Gaylord and S. D. Kevan
Physics Department, University of Oregon, Eugene, Oregon 97403

(Received 28 December 1987; revised manuscript received 26 February 1988)

A band of localized states on the W(110) surface has been observed along $\bar{\Sigma}$ which undergoes a considerable shift to higher binding energy with hydrogen adsorption. We interpret this state and the associated shift in energy to be related to the hydrogen-induced reconstruction of this surface. The change in the nature of the electronic states intrinsic to this surface which result from hydrogen adsorption is fundamental to an understanding of the mechanism which drives this reconstruction.

Surface reconstructions have been observed in a variety of systems.[1-4] Adsorbate-induced reconstructions are of particular interest since this class of reconstructive behavior has direct implications for questions related to bonding of atoms/molecules to surfaces. This is because the perturbations of the substrate electronic structure involved in adsorbate bonding are directly responsible for the geometric rearrangement of the substrate; i.e., a new ground state of the substrate is induced which requires a new geometric configuration. The production of soft-phonon modes, surface strains, etc., which are sometimes invoked as explanations of reconstructive behavior, ultimately result from fundamental changes in the electronic structure of a surface relative to the bulk.

Most reconstructions involve a change in the size of the first substrate layer unit cell. That is, a new unit cell is formed which is larger than that for the unreconstructed surface; e.g., W(001), Ni(110)/H_2.[1,2] However, Chung *et al.* have recently observed that W(110) undergoes a hydrogen-induced reconstruction which can be described as a unidirectional displacement of the top layer atoms with respect to the second-layer along a $\langle\bar{1}10\rangle$.[5] The size of the surface unit cell is unchanged by this transformation, but with respect to the first and second layers, the $(\bar{1}10)$ mirror plane is lost.

Chung *et al.* propose a model to describe the energetics of this reconstruction:[5] The change in the potential energy of the surface tungsten atoms (ΔE_s) is expanded in even powers of the tungsten surface atom displacement along $[\bar{1}10]$. It is assumed that ΔE_s is independent of hydrogen coverage. The potential which binds the adatom is assumed to become asymmetric due to the displacement of the first-layer tungsten. The change in the ground-state energy of the adatom is also described as an even power expansion in the tungsten displacements with the expansion multiplied by the fractional coverage. These assumptions lead to an expression for the total energy of the substrate/adsorbate system which implies that at a critical coverage, instability of the tungsten substrate will set in, and the reconstruction will ensue.

In consideration of the newly proposed reconstruction of this surface, it seems timely to reexamine the hydrogen-induced behavior of W(110) with an emphasis toward an understanding of the driving force for the reconstructive behavior. Therefore, we have performed high-resolution angle-resolved photoemission (ARP) for the clean and hydrogen-covered surface.

A crystal of tungsten was cut and polished with a (110) surface orientation using standard techniques. After introduction of the crystal into the vacuum system, repeated cleaning cycles involving oxidation and sublimation of the oxide were performed (see Refs. 6 and 7). Ultimately, a surface free of contamination (by Auger electron spectroscopy) which exhibited sharp 1×1 low-energy electron-diffraction (LEED) patterns was obtained. Operating pressures of $(0.8-1.2)\times10^{-10}$ Torr were routine. Even in this pressure regime, it was necessary to perform a thermal flash of the sample (to remove CO and H) at 15–20 min intervals to restore the more contamination sensitive features.

Hydrogen exposures were done at room temperature in the form of H_2 either by back filling the chamber or by placing the sample in the line of sight of a channel-plate array doser. The exposures could be reproduced to within 0.01 L (1 L=1 langmuir$=10^{-6}$ Torr sec), but since the H_2 dissociation probability is dependent upon the defect population of the surface, the work-function change was utilized as the indicator of coverage. The work-function change measurements have a precision of ±20 meV which corresponds to a worst case coverage error of 0.07 monolayer.

The ARP experimental system has been described previously.[8,9] High angular and energy resolution experiments can be performed readily with this system. For the experiments described here, *total* instrumental energy resolution was always less than 70 mV [full width at half maximum (FWHM)], and the full angular acceptance was 1° or better. ARP was performed at the National Synchrotron Light Source (NSLS).

Figure 1 shows spectra taken at $k_\parallel=0.62$ Å^{-1} along $\bar{\Gamma}-\bar{H}\equiv\bar{\Sigma}$ (see inset in Fig. 3) for several hydrogen coverages. It is seen that for the clean surface, an asymmetric intensity distribution peaks around 0.3 eV binding energy with respect to the Fermi level. This asymmetric intensity distribution is the result of two overlapping peaks at 0.31 eV (A) and 0.20 eV. As the hydrogen exposure is increased, peak A moves (by about 0.5 eV) to higher binding energy. This behavior was carefully checked and cannot be explained by fitting to two fixed binding-energy peaks of varying intensity. The coverage dependence of

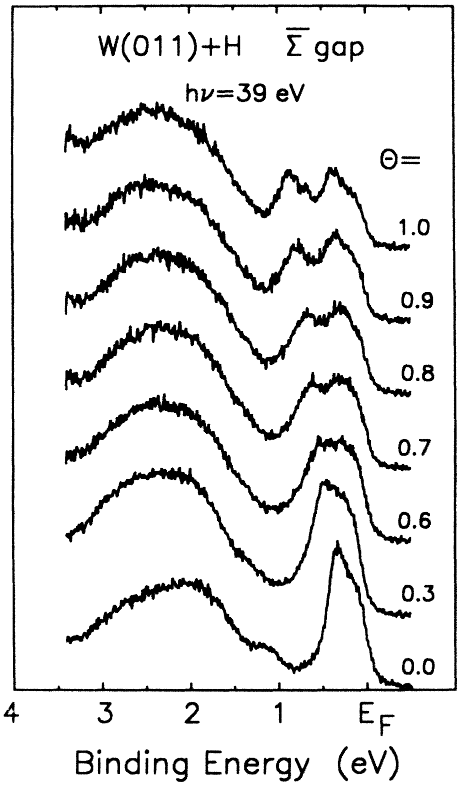

FIG. 1. Valence regime spectra of W(110) taken at $k_{\parallel}=0.62$ Å^{-1} along $\bar{\Sigma}$ vs hydrogen coverage. (Note: Calibration of coverage was done with respect to the work function vs coverage data of Ref. 10.) hν=39 eV, $\vec{A}\parallel\bar{\Sigma}$.

the change in binding energy (Fig. 2) shows two different, approximately linear regimes which cross in the vicinity of 0.4–0.5 monolayer of hydrogen. This is consistent with the idea that a critical coverage is required for the reconstruction,[5] and is in reasonable agreement with the value of the critical coverage at room temperature (0.68 monolayer) determined by Altman *et al.*[11] It should be noted that exact agreement should not be expected, since fluctuations of a short to medium-range nature may occur before the onset of long-range order necessary for observation of the reconstruction by LEED.

The dispersion of state *A* was measured and exhibits a saddle point at $k_{\parallel}=0.56$ Å^{-1} along the $\bar{\Sigma}$ direction. Parallel and perpendicular to $\bar{\Sigma}$ at this $k_{\parallel}$ the bands exhibit nearly parabolic behavior with their common vertex at 0.27 eV binding energy: Parallel to $\bar{\Sigma}$, the state disperses to higher binding energy with an effective mass of $m^* \approx -0.7m_e$. Perpendicular to $\bar{\Sigma}$ the state disperses to lower binding energy with $m^* \approx 0.4m_e$. In each direction, the band *as a whole* is shifted to higher binding energy with hydrogen adsorption. This behavior corresponds to a considerable reduction in the energy of state *A*.

State *A* we believe is surface localized because of the strong shift in its binding energy with hydrogen coverage and because it is rapidly attenuated with oxygen exposure. Further evidence for surface localization is based on consideration of Figs. 3 and 4. Figure 3 shows the (110) surface projected bulk bands of tungsten along the $\bar{\Sigma}$ and $\bar{\Delta}$ ($\equiv\bar{\Gamma}-\bar{N}$) directions. This projection was obtained using a linear combination of atomic orbitals (LCAO) basis with a Slater-Koster interpolation scheme[12] which was modified to include the spin-orbit interaction.[13] A small gap near the Fermi level exists in the vicinity of $k_{\parallel}\approx 0.5$ Å^{-1} along $\bar{\Sigma}$. For obvious reasons, we refer to this as the "$\bar{\Sigma}$-eyeball" gap due to its appearance in the projection of Fig. 3. Figure 4 shows the spectra obtained by changing $k_{\parallel}$ in the $\bar{\Sigma}$ azimuth. State *A* "turns on" at $k_{\parallel}\approx 0.4$ Å^{-1}, rises and then falls in intensity with increasing $k_{\parallel}$ and then "turns off" at $k_{\parallel}\approx 0.8$ Å^{-1}. This is what we expect to observe for a surface localized state; i.e., as $k_{\parallel}$ is set equal to values corresponding to the $\bar{\Sigma}$-eyeball gap the state turns on, while for $k_{\parallel}$ outside the gap, in the bulk continuum, the observed amplitude is small.

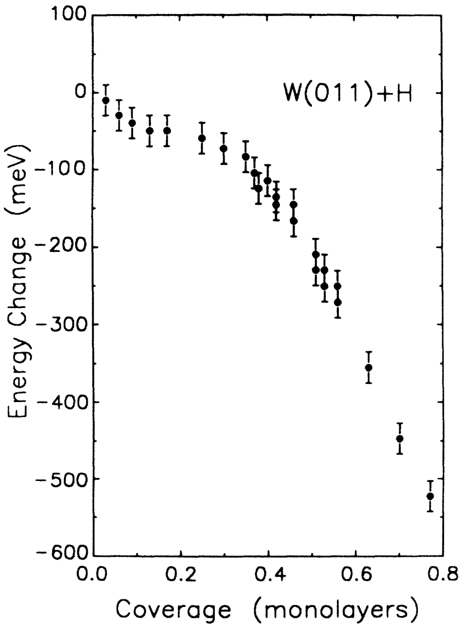

FIG. 2. Binding-energy change of state *A* vs coverage for hydrogen on W(110).

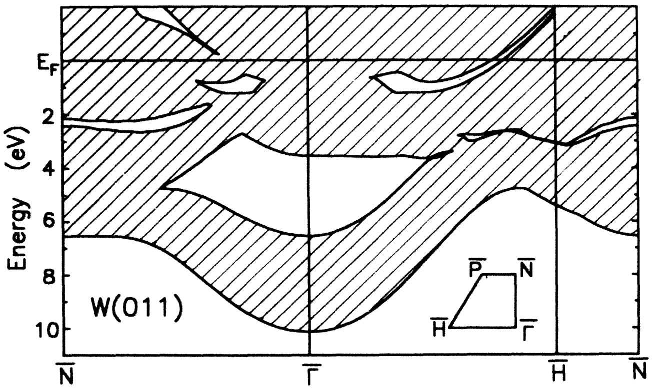

FIG. 3. Surface-projected bulk bands of W(110) along $\bar{\Sigma}$ and $\bar{\Delta}\equiv\bar{\Gamma}-\bar{N}$ (inset shows an irreducible wedge of the first surface Brillouin zone with symmetry points labeled.)

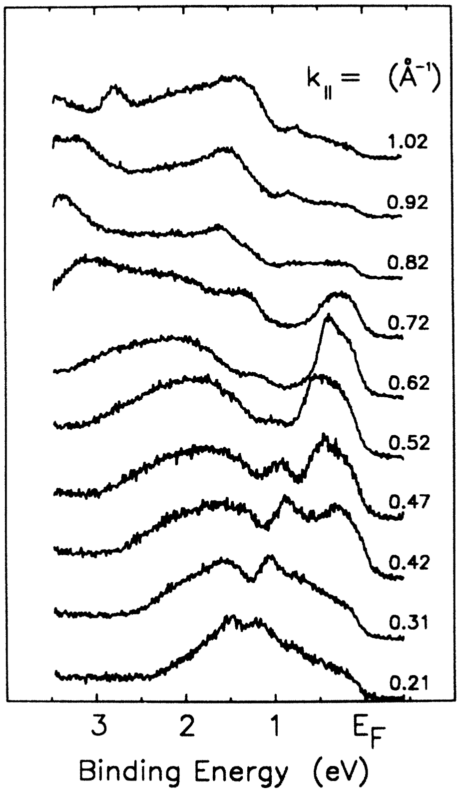

FIG. 4. Valence regime spectra of W(110) vs $k_\parallel$ along $\bar{\Sigma}$; $h\nu = 39$ eV, $\bar{A} \parallel \bar{\Sigma}$.

The observation of a surface localized state which shifts considerably with hydrogen coverage is very interesting with regard to the existence of the hydrogen-induced reconstruction. A translation of the first layer with respect to the second layer would indicate that the balance between first- *to* second-layer bonds which project onto the [$\bar{1}$10] and [001] directions of the surface have been altered as a result of the introduction of hydrogen onto the surface. The energy shift of state *A* is indicative of considerable changes in the orbital character of the state and/or in the extent of its hybridization with other states. Hydrogen adsorption lowers the energy of this surface band which straddles the Fermi level, resulting in a charge redistribution due to the increased number of states below the Fermi level. Moreover, the character of this band is particularly important in terms of first- to second-layer cohesion, due to its location in the eyeball gap. Also, the shift of the state *A* band is rigid. That is, its curvature is unchanged by hydrogen adsorption. This is in keeping with the fact that the first-layer periodicity is not changed by the reconstruction. Only the energy of the state *A* band relative to bulk states is changed. Therefore, the observed behavior of this state, we believe, is related to the driving force for the observed reconstruction of this surface. However, the net contribution of the energy reduction of this state to the lowering of the energy per surface atom will require the measurement of its behavior throughout the Brillouin zone; such a measurement is currently underway. It is interesting to note that the hydrogen-induced reduction of the work function which is observed for this tungsten surface is anomalous with respect to other low-index tungsten surfaces[10] and, indeed, with respect to other transition-metal surfaces.[14] The behavior of state *A* results in charge redistribution in which the change in dipole moment is pointing out of the surface. This would correspond to a reduction of the work function and may be related to the explanation of the anomalous behavior for W(110).

The model of Chung, Ying, and Estrup[5] assumes that ΔE_s or alternatively,[11] the elastic behavior of the substrate, is independent of hydrogen coverage. We believe that this cannot be entirely correct in view of our results. The model for the reconstruction,[5,11] which contains the basic parameters necessary, would provide a more complete description if it were modified to account for the effect of changes of the surface electronic structure. This would require, first, that a coverage dependence of the elastic behavior of the substrate be included. Second, the functional behavior of the displacement-field-dependent change in the chemical potential has to be handled more realistically. That is, the elimination of the chemical potential, in favor of the coverage, could not be done; such an elimination neglects the coverage dependence of the work function of the surface. In general, adsorbate-induced reconstructions should be considered to be caused, in part, by the changes induced in the substrate electronic structure by the adsorbate.

A determination of the relative importance of the effects represented by substrate electronic structure changes and by the changes handled by the model of Chung *et al.*[5,11] will only be attained by further investigation of the properties of this system. We suggest that a measurement of the surface phonon behavior will help to resolve the question of induced changes in the elastic behavior of the surface. Also, one would expect that the induced asymmetry and deepening of the adsorbate binding potential required by their model, will very likely manifest itself in shifts in the energy of the hydrogen vibrational modes on either side of the critical coverage.

This work was carried out in part at the NSLS, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences. Financial support from the U.S. Department of Energy under Grant No. DE-FG06-86ER45275 and from the American Chemical Society Petroleum Research Fund is gratefully acknowledged.

---

[1] T. E. Felter, R. A. Barker, and P. J. Estrup, Phys. Rev. Lett. **38**, 1138 (1977).

[2] T. Engel and K. H. Binder, Surf. Sci. **109**, 140 (1981).

[3] J. R. Noonan and H. L. Davis, J. Vac. Sci. Technol. **16**, 587 (1979), and references therein.

[4] H. D. Shih, F. Jona, D. W. Jepsen, and P. M. Marcus, Phys. Rev. Lett. **46**, 731 (1981).

[5] J. W. Chung, S. C. Ying, and P. J. Estrup, Phys. Rev. Lett. **56**,

749 (1986).

[6] J. A. Becker, E. J. Becker, and P. L. Brandes, J. Appl. Phys. **32**, 411 (1961).

[7] P. W. Tamm and L. D. Schmidt, J. Chem. Phys. **54**, 4775 (1971).

[8] S. D. Kevan, Rev. Sci. Instrum. **54**, 1441 (1983).

[9] P. Thiry, P. A. Bennett, S. D. Kevan, W. A. Royer, E. E. Chaban, J. E. Rowe, and N. V. Smith, Nucl. Instrum. Methods **222**, 85 (1984).

[10] B. D. Barford and R. R. Rye, J. Chem. Phys. **60**, 1046 (1974).

[11] M. Altman, J. W. Chung, P. J. Estrup, J. M. Kosterlitz, J. Prybyla, D. Sahu, and S. C. Ying, J. Vac. Sci. Technol. A **5**, 1045 (1987).

[12] D. A. Papaconstantopoulis, *Handbook of the Band Structure of Elemental Solids* (Plenum, New York, 1986).

[13] J. Friedel, P. Lenglart, and G. Leman, J. Chem. Phys. **25**, 781 (1964).

[14] J. Hölzl and F. K. Schulte, *Solid Surface Physics,* Springer Tracts in Modern Physics, Vol. 85 (Springer, New York, 1979), p. 1.