## Reconstruction of the W(110) Surface Induced by Hydrogen Adsorption

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We report here new LEED data for the H/W(110) surface, showing that W(110) undergoes a reconstruction induced by adsorption of hydrogen above a critical coverage. The structural change consists of a lateral shift of the top layer of W atoms relative to the bulk. We also propose a driving mechanism for the transition which may be important in other chemisorption systems as well. The surfaces most likely to undergo this type of reconstruction are those with adsorption sites consisting of flat potential wells.

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Conventional models of a chemisorbed layer on a metal surface treat the substrate as a static matrix of adsorption sites. Since new bonds are formed in the adsorption, some changes in the atomic geometry of the substrate must occur, but they are usually assumed to be negligible. Among the recognized exceptions are H/Ni(110),<sup>1</sup> H/W(100),<sup>2</sup> and S/Fe(110),<sup>3</sup> which undergo adsorbate-induced reconstruction involving large displacements of metal surface atoms from their positions in the truncated crystal.<sup>4</sup> In these systems, the reconstruction produces a new 2D periodicity and is therefore relatively easily detected by LEED and other techniques. We here report new experimental results for the H/W(110) surface, showing that W(110) also undergoes reconstruction. The structural change consists of a lateral shift of the top layer of W atoms relative to the bulk; since this shift does not alter the dimensions of the surface unit cell, it has escaped detection in previous LEED studies of H/W(110).<sup>5</sup> We also propose a possible driving mechanism for the transition which may be important in other chemisorption systems as well.

The experiments were done on thin ribbons of single-crystal tungsten oriented to the (110) plane. The sample could be cooled to about 80 K by liquid nitrogen and heated resistively to high temperatures. After cleaning in oxygen the crystal was studied in a Video-LEED system which permits simultaneous measurement of the intensity of many diffracted beams.

In agreement with previous investigations,<sup>5,6</sup> hydrogen adsorption at low temperature is found to produce several ordered phases: a  $(1 \times 2)$  structure at coverages  $\theta < 0.5$  monolayer (ML) and a  $(2 \times 2)$  structure at  $\theta > 0.5$  ML. Although the extra LEED beams are sharp, they have low intensity as expected from overlayer structures produced by weakly scattering hydrogen atoms. The  $(1 \times 2)$  and  $(2 \times 2)$  phases disorder at temperatures T > 200 K and T > 250 K, respectively.<sup>6,7</sup>

The new observations, summarized in Fig. 1, concern the symmetry of the substrate. In its clean state the W(110) surface is found to be unreconstructed throughout the accessible temperature range; the surface gives a  $(1 \times 1)$  LEED pattern (see inset in Fig. 1) in which the four integral-order beams,  $0\overline{1}$ ,  $\overline{11}$ , 01,  $1\overline{1}$ , have identical *I-V* (intensity versus beam voltage) curves for normal incidence of the electron beam; this indicates the presence of two perpendicular mirror planes. As seen in Fig. 1, hydrogen adsorption initially does not change the symmetry and all four beams are equally affected. However, at an exposure of approxi-



FIG. 1. Intensity *I* vs exposure for the four integral-order LEED beams shown in the inset (labeled according to the Wood convention). The electron beam energy is V = 62 eV. Curves *a* and *b* show the effect of hydrogen exposure at 85 K on the beam intensities. The effect of oxygen exposure, curve *c*, is the same for all four beams.

mately 2 L [1 L (langmuir) =  $10^{-6}$  Torr sec], corresponding to  $\theta \simeq 0.5$  ML, one of the mirror planes disappears. This effect is not due to the (1×2) to (2×2) transition of the hydrogen overlayer. The data in Fig. 1 were obtained at 85 K, but the same behavior is seen at 300 K, i.e., at a temperature where the overlayer is disordered, the only difference being that the asymmetry sets in at a slightly higher hydrogen exposure. For comparison, Fig. 1 also shows the effect of oxygen adsorption. In this case the symmetry is not altered and the intensities of all four beams follow curve *c* as the oxygen coverage builds up.

There appears to be only one type of structural change consistent with the experimental observations for the effect of hydrogen. It consists of a lateral shift of the top layer of W atoms, as a whole, parallel to the  $\langle 1\bar{1}0 \rangle$  direction. This reconstruction is illustrated in Fig. 2. On a perfect surface, structures generated by shifts to the left- and right-hand side must be equally probable; evidently the degeneracy can be lifted on a real surface, presumably by steps or other defects.





FIG. 2. (a) Unreconstructed W(110) surface. The large solid circles and broken circles show the first and second layer, respectively, of W atoms. The H atoms (small filled circles) are located in the hourglass-shaped sites. The overlayer is disordered at 300 K but forms a  $(1 \times 2)$  structure at low temperature, as illustrated here. The arrows show the translation vectors of the clean surface. The longer vector is parallel to  $\langle 1\bar{1}0 \rangle$ . (b) Reconstructed W(110) surface produced by a shift of the first layer of W atoms to the right-hand side (in the  $\langle 1\bar{1}0 \rangle$  direction). The overlayer of H atoms forms a nonprimitive (2×2) structure (shown here) at low temperature. The reconstruction occurs also at room temperature where the overlayer is disordered.

EELS studies of  $H/W(110)^{8,9}$  have not yet provided an unambiguous determination of the hydrogen adsorption site, but calculations<sup>10</sup> show that at low coverage the adatoms occupy the long-bridge ("hourglass") sites, as illustrated in Fig. 2(a). The proposed reconstruction changes the symmetry of the site, as indicated in Fig. 2(b). This change is probably the reason for the asymmetry observed in photoemission (UPS) studies of this surface,<sup>8</sup> and it offers an explanation for the lack of anisotropy in the hydrogen diffusion coefficient at high coverage.<sup>11</sup>

The driving mechanism for the hydrogen-induced reconstruction of W(110) can be understood by consideration of the change in energy of the adatom in a distorted well. Let u represent the displacement of a surface W atom along the  $\langle 1\overline{10} \rangle$  direction in the reconstruction. The clean W(110) surface is stable against this reconstruction and its potential energy  $E_s$  (per surface W atom) can be expanded in powers of u. To fourth power in u, we have

$$\Delta E_s = \alpha_1 u^2 + \alpha_2 u^4, \quad \alpha_1, \alpha_2 > 0. \tag{1}$$

After the reconstruction, the symmetry of the H adsorption site changes and the potential  $U(\mathbf{r})$  of the adsorbed H near the adsorption site also changes. Figure 3(a) illustrates schematically a cross section of the po-



FIG. 3. Qualitative diagram of the potential energy of an H atom adsorbed in the hourglass site (see Fig. 2). The distance x is parallel to  $\langle 1\overline{10} \rangle$ . (a) Unreconstructed surface. (b) Reconstructed surface.

tential before the reconstruction showing the variation of  $U(\mathbf{r})$  along the  $\langle 1\overline{1}0 \rangle$  direction, and Fig. 3(b) shows what happens after the reconstruction. Previous calculations<sup>10</sup> have shown that for H/W(110),  $U(\mathbf{r})$ has a flat region in the center of the hourglass-shaped adsorption site. We demonstrate here that this feature implies a large increase in the binding energy of H atoms upon a lateral shift of the first layer. Thus the surface will be driven to reconstruct when the hydrogen coverage exceeds a critical value,  $\theta_c$ . Upon reconstruction, the change  $\Delta U(\mathbf{r})$  can be expanded to  $u^2$  as

$$\Delta U(\mathbf{r}) = \frac{\partial U_1(\mathbf{r})}{\partial x} u + \frac{1}{2} \frac{\partial^2 U_1(\mathbf{r})}{\partial x^2} u^2.$$
(2)

Here x denotes the  $\langle 110 \rangle$  direction, and  $U_1(\mathbf{r})$  is the contribution to  $U(\mathbf{r})$  from the first substrate layer. The change in the ground-state energy of an adatom has the corresponding expansion in  $u_1$ ,

$$\Delta \epsilon_0 = -\beta_1 u^2 + \beta_2 u^4. \tag{3}$$

 $\beta_1$  is determined by second-order perturbation:

$$\beta_{1} = -\frac{1}{2} \langle \psi_{0} | \frac{\partial^{2} U_{1}(\mathbf{r})}{\partial x^{2}} | \psi_{0} \rangle + \sum_{n} \frac{|\langle \psi_{n} | [\partial U_{1}(\mathbf{r}) / \partial x] | \psi_{0} \rangle|^{2}}{\epsilon_{n} - \epsilon_{0}}, \quad (4)$$

where  $|\psi_0\rangle$ ,  $|\psi_n\rangle$ ,  $\epsilon_0$ , and  $\epsilon_n$  represent the groundstate and excited-state eigenfunctions and eigenvalues of the adatom in the unperturbed potential  $U(\mathbf{r})$ . To lowest order in the coverage (defined as the number of adatoms divided by the number of surface W atoms), we can neglect the H-H interaction, and the total change in ground-state energy of adatoms (per surface W atom) can be written as

$$\Delta E_a = \theta \left( -\beta_1 u^2 + \beta_2 u^4 \right). \tag{5}$$

The important point to note here is that the flatness of the potential  $U(\mathbf{r})$  implies small energy differences between the first few eigenstates, which in turn causes the second-order term in (4) to dominate over the first-order term, leading to a large and positive value for  $\beta_1$ , and hence a lowering in the total energy of the adsorption system. The sign of the higher-order term  $\beta_2 u^4$  is more difficult to estimate but it is not essential for our discussion here. Equations (1) and (5) together give the total change in energy  $\Delta E_{tot} = \Delta E_s + \Delta E_a$  as

$$\Delta E_{\text{tot}} = (\alpha_1 - \beta_1 \theta) u^2 + (\alpha_2 + \beta_2 \theta) u^4.$$
 (6)

This implies the existence of a critical coverage  $\theta_c = \alpha_1/\beta_1$ . For  $\theta > \theta_c$ , the surface is unstable against the proposed reconstruction involving the lateral shift. Note that to this order in  $\theta$ ,  $\Delta E_{\text{tot}}$  is independent of the structure of the overlayer. Thus the reconstruction

tion of the surface is predicted to occur for an ordered as well as a disordered H overlayer. (When terms of higher order in  $\theta$  are included a correlation between the overlayer transition and the substrate reconstruction may exist.<sup>12</sup>) At elevated temperatures, population of higher states would lead to a smaller value of  $\beta_1$  and hence a larger critical coverage. These findings are in qualitative agreement with the experimental data. Further tests of the model should include a full surface-structure analysis, more detailed measurements of the (weak) temperature dependence of the reconstruction, and an investigation of possible hydrogen isotope effects.

In conclusion, hydrogen adsorption on W(110) is found to induce a structural transformation of the metal surface. The transition is characterized not by the appearance of a new periodicity but by a lowering of the surface symmetry which is interpreted as due to a reconstruction consisting of a lateral shift of the topmost tungsten layer. The driving mechanism can be understood in terms of the change in the hydrogen binding energy caused by the distortion of the adatom potential well. Although we have presented a quantum mechanical theory here, the same qualitative effect persists in the classical regime. The crucial ingredient required is a flat adsorption potential well due to a balance between the contributions from the topmost substrate layer and the subsurface layer. The lateral shift of the first layer changes this balance, leading to a large change in energy. This model is sufficiently general to make it plausible that a similar reconstruction occurs in many other chemisorption systems.

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 $^{3}H.$  D. Shih, F. Jona, D. W. Jepsen, and P. M. Marcus, Phys. Rev. Lett. **46**, 731 (1981).

<sup>4</sup>P. J. Estrup, in *Chemistry and Physics of Solid Surfaces V*, edited by R. Vanselow and R. Howe (Springer, New York, 1984), p. 205.

<sup>5</sup>V. V. Gonchar, O. V. Kanash, A. G. Naumovets, and A. G. Fedorus, Pis'ma Zh. Eksp. Teor. Fiz. **28**, 358 (1978) [JETP Lett. **28**, 330 (1978)]; V. V. Gonchar, Uy M. Kagan,

<sup>&</sup>lt;sup>1</sup>T. Engel and K. H. Binder, Surf. Sci. **109**, 140 (1981); V. Penka, K. Christmann, and G. Ertl, Surf. Sci. **136**, 307 (1984).

 $<sup>{}^{2}</sup>R.$  A. Barker and P. J. Estrup, Phys. Rev. Lett. **41**, 130 (1978); I. Stensgaard, L. C. Feldman, and P. J. Silverman, Phys. Rev. Lett. **42**, 247 (1979); D. A. King and G. Thomas, Surf. Sci. **92**, 201 (1980).

O. U. Kanash, A. G. Naumovets, and A. G. Fedorus, Zh. Eksp. Teor. Fiz. 84, 249 (1983) [Sov. Phys. JETP 57, 142 (1983)].

<sup>6</sup>I. F. Lyksyutov and A. G. Fedorus, Zh. Eksp. Teor. Fiz. **80**, 2511 (1981) [Sov. Phys. JETP **53**, 1317 (1981)].

<sup>7</sup>L. D. Roelofs and P. J. Estrup, Surf. Sci. **125**, 51 (1983). <sup>8</sup>G. B. Blanchet, N. J. Dinardo, and E. W. Plummer, Surf.

Sci. 118, 496 (1982).

<sup>9</sup>B. M. Davies and J. L. Erskine, J. Electron Spectrosc. 29, 323 (1983).

 $^{10}\text{S.}$  Holloway, P. Nordlander, and J. Norskov, Surf. Sci. 136, 327 (1984).

<sup>11</sup>M. Tringides and R. Gomer, Surf. Sci. **155**, 254 (1985); S. C. Wang and R. Gomer, J. Chem. Phys. **83**, 4193 (1985).

 $^{12}\text{D.}$  Sahu, S. C. Ying, and J. M. Kosterlitz, to be published.