Summary Abstract: X-ray diffraction study of multilayer W(001) surface reconstruction

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The clean W(001) surface undergoes a reconstruction upon cooling below 300 K which produces a $(\sqrt{2}\times\sqrt{2})R\,45°$ two-dimensional periodicity.[1] Systematic extinctions in the low-energy electron diffraction (LEED) pattern show that surface W atoms are laterally displaced in the ⟨110⟩ directions in the reconstructed phase.[2,3] A detailed model of the surface geometry has been developed, based largely on LEED intensity analyses,[4,5] and has been used in numerous calculations of the stability of this surface.[6] Displacements of only top-layer atoms, however, have been considered in these studies. In the present work, we have extended previous surface x-ray diffraction techniques,[7] by using nongrazing geometry, to allow study of the three-dimensional character of the reconstructed W(001) surface.

Grazing incidence x-ray crystallography, which studies surface structures in two-dimensional projection, has proven to be a valuable complement to LEED. The advantage of x-ray diffraction over LEED for surface crystallography is that the x-ray intensities may be analyzed with straightforward kinematical theory. The grazing geometry has been employed in order to enhance the signal by total external reflection and by resolution effects, and to reduce contributions from the bulk. In this geometry, the perpendicular momentum transfer is restricted approximately to zero, i.e.,

$$q_\perp \equiv (2\pi/a_0)l \simeq 0,$$

($a_0 = 3.16$ Å is the W lattice parameter). In the case of a reconstructed surface this is not necessary because coherent scattering from the bulk is not allowed along the extra fractional-order reciprocal lattice "rods." So $q_\perp$ can be made relatively large, and out-of-plane structural features may be properly studied. Generally, large incident x-ray intensities are required, but in the present experiment a 60-kW rotating anode x-ray source proved to be adequate due to the large scattering power of tungsten and the magnitude of the surface atom displacements.

If the W(001) reconstruction were confined to a single layer as in the current model, no variation of the diffracted intensity should occur as l is increased, i.e., along a reciprocal lattice rod, except for the gradual decline due to the W atomic scattering factor and to the Debye–Waller factor. Contrary to this expectation, the x-ray measurements reveal a pronounced modulation along each of the four rods $(\frac{1}{2},\frac{1}{2},l)$, $(\frac{1}{2},\frac{3}{2},l)$, $(\frac{3}{2},\frac{3}{2},l)$, and $(\frac{3}{2},\frac{5}{2},l)$. Figure 1 shows the intensities integrated over the sample mosaic spread with background substracted, and corrected for the Lorentz factor, polarization, active sample area, and resolution effects. It should be noted that the resolution correction has not been applied in previous surface structural work confined to in-plane analysis; it comes about because of the progressive tilting of the rods with respect to the instrumental resolution function at larger values of l. This correction accounts for a loss of integrated intensity along the rods and correctly describes the broadening of the radial linewidths observed.[8] The sharp intensity maxima at small values of perpendicular momentum transfer, seen in Fig. 1, are the characteristic peaks due to refraction effects near the critical angle of total external reflection.[9]

Two possible explanations of the observed oscillatory l dependence of intensity have been ruled out. First, a one-layer buckled model would require an unacceptably large buckling amplitude of $a_0/4$. Secondly, if the surface were stepped, modulation of peak intensity along the rods could

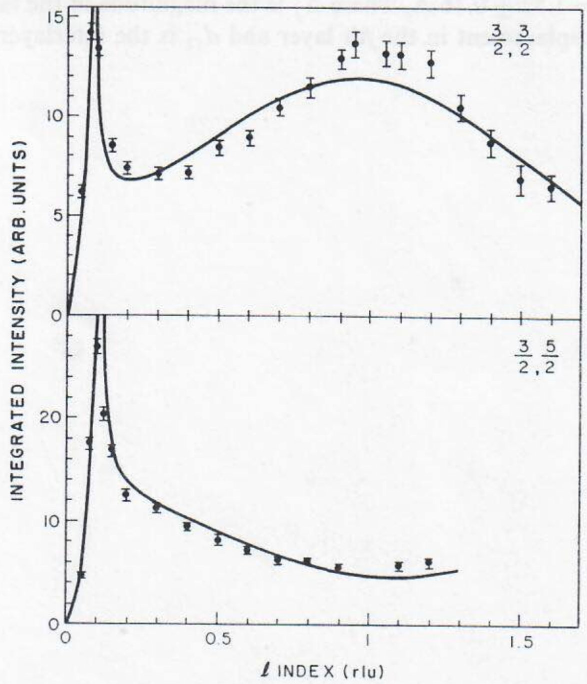

FIG. 1. Modulation of integrated intensity along rods for $(h,k) = (\frac{3}{2},\frac{3}{2})$ (top) and $(h,k) = (\frac{3}{2},\frac{5}{2})$ (bottom). The data were taken at $T = 175$ K. The solid curve is the best fit from the proposed two-layer model with structural parameters $\Delta_1 = 0.24 \pm 0.025$ Å, $\Delta_2 = 0.046 \pm 0.016$ Å, and $d_{12} = 1.52 \pm 0.16$ Å.

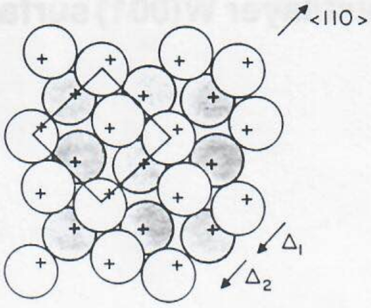

FIG. 2. Top view of atomic displacements from bulk terminated positions (+) for the proposed two-layer model of reconstruction. The top-layer displacements Δ_1 and second-layer displacements Δ_2 are along the [110] forming zig-zag chains in each layer along the [$1\bar{1}0$]. The shaded atoms are in the second layer.

result. But these steps would also act to modulate the rod widths[10] in such a way as to conserve the integrated intensity. No such width modulation was observed.

The remaining possibility is that multilayer reconstruction occurs. We have extended the current model, in which top-layer atoms are laterally displaced to form zig-zag chains, by including lateral second-layer atomic displacements in the same fashion as the top layer. This structure explains well both the relative intensities of different order rods and the phase of intensity modulation between rods having $(h+k)$ even and $(h+k)$ odd, provided that an atom in the top layer and its neighbors in the second layer along [110] are displaced in the same direction (Fig. 2). The best-fit structural parameters from a least-squares analysis are $\Delta_1 = 0.24 \pm 0.025$ Å, $\Delta_2 = 0.046 \pm 0.016$ Å, and $d_{12} = 1.52 \pm 0.16$ Å, where Δ_j is the magnitude of the lateral displacement in the jth layer and d_{12} is the interlayer distance. Figure 1 shows the corresponding fit to the experimental data.

The inclusion of second-layer displacements in the model of the reconstructed structure will affect the interpretation of both theoretical and experimental results. The discrepancy between total energy calculations,[6] which indicate the absence of interlayer contraction, and the present data, which yield a 4% contraction, may be resolved in this manner. More importantly, multilayer reconstruction should further stabilize this phase.[11] The agreement between our results for Δ_1 and d_{12} with those of LEED,[5] which gives $\Delta_1 = 0.16$ Å and $d_{12} = 1.49$ Å is quite good but it will clearly be of interest to repeat the LEED analysis using the modified W(001) structure.

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