Reconstruction of the W(001) Surface and Its Reordering by Hydrogen Adsorption, Studied by MeV Ion Scattering

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High-energy ion scattering in combination with channeling has been used to study the W(001) +hydrogen surface. It is shown conclusively that the clean W(001) and the W(001)$c(2\times2)$H surfaces are reconstructed at room temperature, that the surface reorders by H saturation, and that two models proposed for the $c(2\times2)$ surface structure are not valid. Furthermore we have obtained absolute coverage data [for the W(001) + D_2 system] using a nuclear reaction technique.

Although the interaction of hydrogen with the W(001) surface has been the object of numerous studies, many uncertainties have persisted.[1] Among these are the exact nature of the clean surface, the possible effects of hydrogen adsorption on the substrate, and the correlation between hydrogen coverage and the observed low-energy electron-diffraction (LEED) pattern.

At room temperature the LEED pattern from a cleaned W(001) surface shows weak and diffuse half-order spots corresponding to a $c(2\times2)$ structure. Recent investigations[2,3] have concluded that these spots are not due to residual surface impurities, indicating indirectly that the clean surface is reconstructed. By hydrogen adsorption (or by crystal cooling) the diffraction pattern develops into a full $c(2\times2)$ structure. There is considerable interest in establishing whether the half-order spots are due to scattering from adsorbed H atoms or due to an adsorbate-induced surface transformation. Some support for the second possibility was obtained recently[4] by noting the difficulty in getting agreement between measured LEED intensity spectra and spectra calculated for H atoms adsorbed on an unperturbed surface. At higher H coverages the half-order spots split into four, become streaky, and finally disappear to give a $p(1\times1)$ pattern at saturation.

In contrast to LEED, high-energy ion scattering in combination with channeling[5] does not require long-range order and it is in general possible to distinguish between backscattered intensities from the substrate and from the adsorbate. It is therefore possible to study the W surface structure directly and obtain structure information even in cases where the LEED pattern is poorly developed. We show conclusively that the clean W(001) and the W(001)$c(2\times2)$H surfaces are reconstructed at room temperature, that the surface reorders by H saturation, and that two models proposed for the $c(2\times2)$ surface structure are not valid.

The ultrahigh-vacuum system, equipped for Auger electron spectroscopy and LEED and coupled to an ion accelerator, has been described previously.[6] The clean W(001) surface was prepared using standard techniques including heating in O_2 and flashes to ~2400 K. The observed sequence of H (or D) induced-LEED patterns mentioned above correspond to observations by other groups[2,3] giving further evidence for the surface perfection since small amounts of impurities are known to inhibit the transformation.

Two typical backscattering spectra are shown in Fig. 1. It is evident from these that the adsorption of H causes a significant decrease in the backscattering yield from the surface. This indicates that fewer W surface atoms are exposed to the incoming beam when the surface is H saturated than when it is clean. With the use of proper background-subtraction techniques[6,7] the surface-peak yield can be transformed into an equivalent effective number of atoms per row.[8] Figure 2 shows the yield as a function of H exposure and the corresponding observed LEED pattern. It should be noted that the above results for the $\langle 111\rangle$ axis alone could be explained by assuming a considerable surface relaxation in the clean state which disappears upon H adsorption. Results obtained at normal incidence, however, were quite analogous, indicating a lateral component of motion of the W atoms. A summary of surface-peak intensities in units of atoms per row at different energies and directions of incidence is given in Table I.

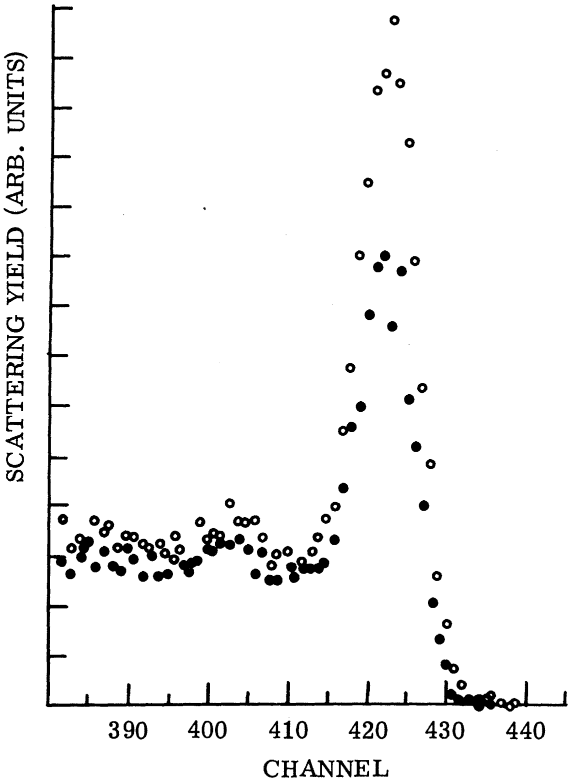

FIG. 1. Backscattered energy spectra from W(001) for 1-MeV He$^+$ incident in the ⟨111⟩ direction, for a clean (open circles) and hydrogen-saturated surface (filled circles).

TABLE I. Surface-peak intensities in units of atoms per row.

	Energy (MeV)	Clean or $c(2\times2)$	H Sat.	Model calc.
⟨001⟩	0.6	1.36	1.05	1.07
	1	1.60	1.22	1.21
	2	1.99	1.65	1.55
⟨111⟩	0.6	1.85	1.14	1.11
	1	2.07	1.41	1.30
	2	2.61	1.96	1.74
Uncertainty		~5%	~5%	~2%

By adsorbing deuterium instead of hydrogen and using the nuclear reaction $D(^3He, H)^4He$, which has a known cross section,[9] the ion-beam-induced desorption cross section and the D coverage as a function of exposure could be studied. The desorption cross section for the saturated state of D on W(001) under 700-keV $^3He^+$ bombardment was determined to be $\sim 4\times10^{-18}$ cm^2. Since typical ion doses for data points in the backscattering experiments were ~1 μC/mm^2 ion-beam-induced H desorption could be neglected.

Figure 3 shows a typical uptake curve. The experimental points have been fitted with an exponential assuming a $(1-\theta)$ coverage dependence of the adsorption kinetics. It is noteworthy here that the curve passes through the origin. As a result of the intentional gas exposure, the partial pressure of deuterium was higher than that of hydrogen during these measurements, yet no deuterium was detected on the surface after a flash, establishing a lower limit on the deuterium coverage of $\sim 10^{13}$ atoms/cm^2. The reaction technique sums the deuterium in the first ~2000

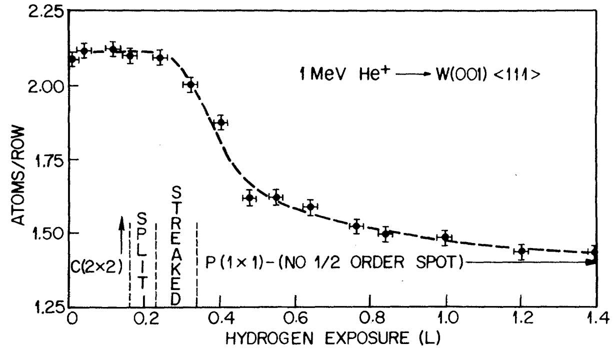

FIG. 2. Intensity of the surface peak for the ⟨111⟩ direction as a function of hydrogen exposure. The symmetry of the LEED pattern and description of the $\frac{1}{2}$-order spots in indicated as a function of coverage. For the region marked $c(2\times2)$ the $\frac{1}{2}$-order spots are initially very diffuse and reach a maximum intensity around the indicated arrow.

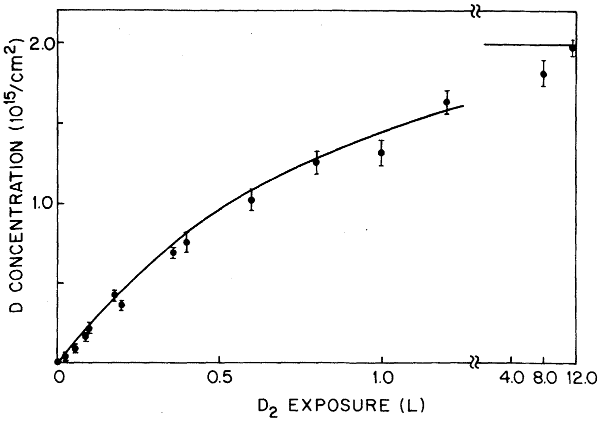

FIG. 3. Coverage curve for the deuterium uptake on W(001). The full curve is an exponential discussed in the text.

Å of the crystal. It is concluded that the diffuse spots in the clean-crystal pattern are not due to residual hydrogen and that the $c(2\times2)$ structure observed at lower temperature cannot be due to any diffusion of hydrogen from the bulk as once suggested.[10] From the uptake curve and similar measurements a saturation coverage of $(2.0\pm0.2)\times10^{15}$ atoms/cm^2 was determined. This agrees well with the only previous direct measurement based on a calibrated-flux molecular-beam experiment.[11]

The significant reduction in backscattering yield from the surface after hydrogen saturation is a direct indication that the clean W(001) surface is reconstructed. Figure 2 and equivalent results for normal incidence shows that the surface remains reconstructed for H coverages beyond the $c(2\times2)$ state with split, streaky spots, i.e., that the extra spots in the LEED pattern are due to an adsorbate-induced surface transformation.

The third column in Table I shows results obtained by computer simulations[7] assuming the surface to be a simple termination of the bulk (no reconstruction or relaxation). The good agreement between these results and the results for the H-saturated surface allows us to conclude that the H-saturated W(001) surface is nonreconstructed.[12] A more detailed computer model calculation sets an upper limit of ~4% on the possible relaxation in the H-saturated state. A previous ion-scattering study[6] set an upper limit on the clean-surface relaxation at ~6%.

It is noted from Table I that the change in scattering yield by H saturation is ~0.34 atoms/row for normal incidence and ~0.67 atoms/row for ⟨111⟩ incidence. Simple crystallographic considerations show that this ratio (1:2) is to be expected for displacements which are not aligned with the directions of incidence. Within the uncertainties there is no energy dependence in the difference in number of exposed atoms for clean and H-saturated surfaces. This indicates that the atoms which take part in the reconstruction are displaced so much that the second atom along the row is outside the shadow cone from the first atom for all energies used. Since the shadow cone in the 600-keV case is ~0.2 Å, this sets the lower limit on the displacements in the clean and $c(2\times2)$H state.

The detailed nature of the reconstruction model is not yet understood. It is evident from the present measurements, however, that the two models proposed so far for the W(001)$c(2\times2)$ structure cannot represent the true situation. Although these models were originally proposed for the cooling-induced transformation it is reasonable to compare them to the room-temperature results for both clean and $c(2\times2)$H states. The cooling transition is not sharp and it has been shown that the room-temperature $c(2\times2)$H and cooled $c(2\times2)$ surfaces give similar LEED intensity spectra.[4]

One model assumes the $c(2\times2)$ structure to be a result of perpendicular shifts with alternate surface atoms displaced up and down.[2] This model can be ruled out since the surface scattering at normal incidence would not be significantly increased for this type of reconstruction.

Structures of $c(2\times2)$ symmetry can easily be constructed from models in which all or $\frac{1}{2}$ of the surface atoms are allowed to be displaced. An example of the former is the parallel-shift model where all the surface atoms are moved to form zigzag chains along the ⟨11⟩ directions in the surface.[3] From the ion-scattering results only ~67% of the surface atoms appear to be displaced. In light of the symmetry considerations mentioned above, we consider factors which can influence this value. Computer simulations show that in some cases the apparent (measured) fraction of displaced atoms exceeds the actual one due to flux-peaking effects. (In the present case, for example, 50% of the surface atoms displaced laterally by 2.5 Å would appear as ~60% at normal incidence.) The shadowing effect of the adsorbed H is negligible but changes in the surface defect structures or vibration amplitudes by H adsorption could contribute to the measured yield difference thereby reducing the fraction of displaced atoms, or, the reconstruction could involve more than the surface layer. In fact, although we can speculate on factors which would make displacement structures with $\frac{1}{2}$ the surface atoms displaced consistent with the ion-scattering data, we cannot envision a process whereby a full monolayer of displacements would appear considerably lower. We conclude that models with all surface atoms displaced are inconsistent with the ion-scattering data.

We do not at the moment propose any detailed model consistent with both the LEED and the ion-scattering data. To explain the initial change in the LEED pattern during hydrogen adsorption we suggest a situation in which the W surface atoms participating in the reconstruction are already displaced on the clean surface but in a more or less random manner corresponding to small domains. H adsorption (or cooling) increases the long-range order giving sharper spots. At the same time a change in displacement may occur to account for the higher intensity in the half-order spots. Another consideration involves the charge-density-wave mechanism originally proposed by Felter, Barker, and Estrup[2] for the clean surface and discussed recently by Tosatti.[13] It is possible that the hydrogen coverage induces changes on the two-dimensional Fermi surface yielding initially a change in the first monolayer distortion pattern from an incommensurate to a commensurate structure corresponding to the sharp $c(2\times2)$ pattern, and then finally to the $p(1\times1)$ pattern.[13,14]

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[1] See, for example, L. D. Schmidt, in *Interaction on Metal Surfaces*, edited by R. Gomer (Springer, New York, 1975), p. 63; E. W. Plummer, *ibid.*, p. 143.

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

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[5] E. Bøgh, in *Channeling*, edited by D. V. Morgan (Wiley, London, 1973), p. 435.

[6] L. C. Feldman, R. L. Kauffman, P. J. Silverman, R. A. Zuhr, and J. H. Barrett, Phys. Rev. Lett. 39, 38 (1977).

[7] I. Stensgaard, P. J. Silverman, and L. C. Feldman, to be published.

[8] The unit atoms per row is convenient for comparison to calculations. Consider, for example, normal incidence on W(001). Of the ⟨001⟩ rows half have their first atom in the surface layer, and half in the second layer, each layer having a density of 1×10^{15} atoms/cm^2. In this case 1 atom/row is therefore 2×10^{15} atoms/cm^2.

[9] L. C. Feldman and S. T. Picraux, in *Ion Beam Handbook for Material Analysis*, edited by J. W. Mayer and E. Rimini (Academic, New York, 1977), p. 112.

[10] K. Yonehara and L. D. Schmidt, Surf. Sci. 25, 238 (1971).

[11] T. E. Madey, Surf. Sci. 36, 281 (1973).

[12] A comparison in Ref. 8 showed that measured surface-peak intensities are in general slightly higher than calculated values. The higher scattering yield has been explained by enhanced surface-vibration amplitudes. The present work indicates that in one case (Ref. 6) at least part of the reason is the reconstructed surface phase. Existing data are insufficient to conclude that the ion-scattering results should always show an excess. Although the influence of the adsorbed H on the surface vibrational amplitude is assumed small, it is conceivable that adsorption removes some soft-phonon modes parallel to the surface, bringing the experimental value closer to the calculation.

[13] E. Tosatti, Solid State Commun. 25, 637 (1978).

[14] S. T. Chui, to be published.

Saturation of the 9.4-GHz Hypersonic Attenuation in Fast-Neutron-Irradiated Crystalline Quartz

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Saturation of the 9.4-GHz hypersonic attenuation was observed in crystalline quartz after fast-neutron irradiation. The sample, which exhibits long-range order, shows a low-temperature acoustic behavior similar to that observed in amorphous materials. As in glasses, the results can be explained by the existence of configurational low-energy excitations, with a two-state nature, which were put forward as intrinsic to the amorphous state.

In this Letter, I report observations[1] of the saturation of the high-frequency acoustic attenuation in a crystal, possessing long-range order, which are similar to the acoustic anomalies in glasses.[2-6] A quartz crystal was neutron irradiated, producing localized defects which we believe to be the elusive two-level systems (2LS) hypothesized for glasses.[7,8] Furthermore, I present additional evidence for a certain microscopic picture for the localized low-energy excitations which cause the anomalies: The elongated Si-O-Si bond with two equilibrium positions