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New low-energy-electron-diffraction fine structure on W(110) and effect of hydrogen chemisorption

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High-resolution low-energy-electron-diffraction (LEED) measurements of the specular beam from W(110) are presented. A new LEED fine structure associated with the $(\bar{2}0)$ beam threshold is observed and studied in detail. The evolution of this feature under hydrogen chemisorption is also examined. Modification of the fine-structure line shape with gas coverage is explained by a gradual change in the scattering properties of the substrate rather than by a transformation of its surface potential barrier. The strengthening of the fine structure with gas exposure could be indicative of an ordered chemisorption in an interstitial site for hydrogen on W(110).

Low-energy-electron-diffraction (LEED) intensity curves at low energy are often characterized by rapid fluctuations caused by the scattering from the surface potential barrier (SPB).[1] This fine structure results from the superposition of a directly reflected wave and a wave reflected after being temporarily trapped between the substrate and the surface barrier in a pre-emergent diffracted beam. This phenomenon was originally called electronic surface resonance[2] because this trapped wave was believed to produce quasistationary surface states above vacuum level. However, recent analyses[3-7] demonstrate that in most cases the pre-emergent beam is reflected only once at the SPB, and so the mechanism producing fine structure is rather interference. The main interest of LEED fine structures is that their analysis yields information on the nature of the SPB of metals. For example, the location of the origin of the long-range image potential[8] and its saturation close to the substrate[3-5] have been established on several crystals by the study of LEED fine structure.

The physical mechanism leading to LEED fine structures being understood, their detailed study is now undertaken. The angular behavior of these features,[9] their spin dependence,[6] and their sensitivity to gas adsorption[10,11] are different aspects now being considered. However, in the latter case, the absence of high-resolution studies precludes a detailed analysis of the influence of gas adsorption on the SPB. In this Communication, we present a high-resolution study of a new LEED fine structure observed on W(110). The influence of hydrogen adsorption on this feature is examined leading to interesting observations and conclusions.

The experimental setup is the same as that used in our previous study of W(110).[9] However, for the present measurements, the azimuth angle of the crystal has been rotated by 90° so that the incident plane now contains the short axis of the real conventional rectangular net. The energy resolution is 12–15 meV for an impact energy of 15 eV. The base pressure of the system is limited by a small real leak to a value of 3×10^{-10} Torr. High-purity hydrogen is introduced by means of a variable leak. When monitoring with a quadrupole mass spectrometer during typical gas exposures it is found that the dominant contaminant, nitrogen, represents less than 3% of the residual gas. All measurements are performed at room temperature. However, the heat produced by the spectrometer electron gun raises the crystal temperature to about 320 K during operation. The crystal sample is cleaned by flashing at 2400 K. No supplementary oxygen annealings are performed for this experiment.

The LEED fine structure is observed in the specular beam and is associated with the $(\bar{2}0)$ beam threshold [or the $(-4\pi/a,0)$ reciprocal-lattice rod]. Figure 1 reproduces two typical spectra measured for polar angles of incidence $\theta_i=70°$(a) and 85°(b). The typical Rydberg-like oscillations associated with the long-range image force[12] are well defined at large angles of incidence but become progressively blurred at lower angles. Below $\theta_i=65°$ the fine structure is hardly detectable. In the frame of the four-beam approximation,[1] the amplitude of the (00) beam below the emergence of the beam g can be written[4]

$$T(0,0)=T_c(0,0)\left[1+\frac{RS(g,g)}{1-T_c(g,g)S(g,g)}\right] , \quad (1)$$

where

$$R=\frac{T_c(0,g)\,T_c(g,0)}{T_c(0,0)} . \quad (2)$$

Here $T_c(0,0)$, $T_c(g,g)$, $S(g,g)$, and R are complex numbers representing reflexion of the beams (00) and g at the substrate, reflection of g at the barrier,

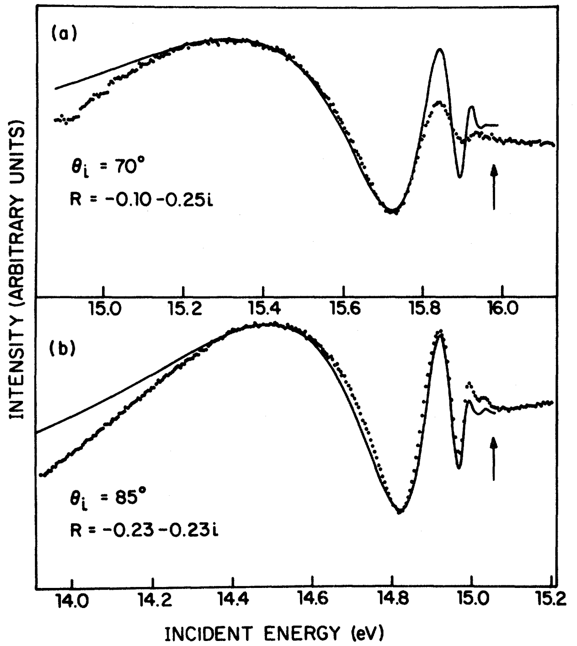

FIG. 1. LEED fine structure in the specular beam on W(110) in the [10] azimuth for two angles of incidence, and the corresponding calculated profiles obtained from Eq. (1) after numerical broadening. Value of the parameter R used for the fit is given for each curve. Energy scale is adjusted so that the $(\bar{2}0)$ beam threshold (indicated by an arrow) corresponds to its theoretical value for the given angles.

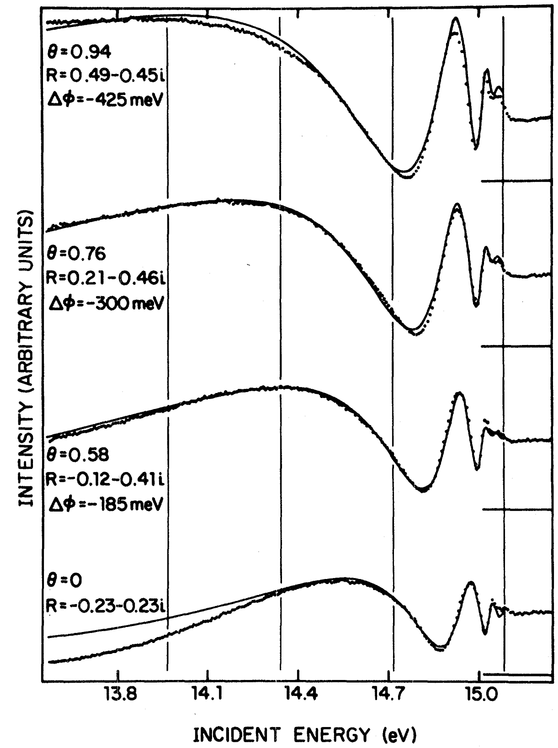

FIG. 2. Evolution of LEED fine structure at $\theta_i = 85°$ during hydrogen chemisorption, and the corresponding calculated profiles. Curves recorded after hydrogen chemisorption are shifted to higher energy by the value of the corresponding work-function change $\Delta\phi$ as indicated.

and the coupling factor between g and (00). A surface resonance arises when the denominator in (2) reaches or approaches zero. This situation leads to the formation of quasistationary states which cause strong fluctuations in the (00) beam when decaying. In the case studied here, it appears that this situation does not prevail. In fact, by putting $T_c(g,g) = 0$ in Eq. (1) it is possible to obtain good fits of the experimental data as illustrated in Fig. 1. The fits are obtained by taking R as an adjustable parameter and $S(g,g)$ as the coefficient of reflection of a classical image barrier.[4,13] The excellent accuracy of the fit at $\theta_i = 85°$ seems to indicate that saturation effects are less important for scattering at large angle of incidence in accordance with previous results.[4] In view of previous studies performed with the present apparatus,[9,14] the damping of the higher-order Rydberg fringes at low angle cannot be of instrumental origin but rather is the indication of an angular or energy dependence of the diffuse scattering at the surface. Measurements of the fine structure at several angles above $\theta_i = 65°$ show that the peaks and dips of the profile follow a two-dimensional free-electron dispersion. However, a small deviation from the law is observed for the first peak.

The variation of LEED fine structure as the result of hydrogen chemisorption is also studied. Gas exposure L is calculated by the p^*x time product with p^* the pressure corrected for gauge sensitivity. The coverage θ is then deduced from the θ-vs-L plot of Barford and Rye.[15] The validity of such a procedure is checked by work-function change ($\Delta\phi$) measurements during coverage which are in good agreement with the $\Delta\phi$-vs-θ curve of Barford and Rye.[15] $\Delta\phi$ measurements were achieved by recording the $(\bar{2}0)$ beam threshold displacement with exposure. The accuracy of this technique is about ±5 meV and because of its simplicity it could well be applied to other surfaces for which LEED fine structure exits. At saturation [$\sim$85 L (1 L = 10^{-6} Torr sec)], the total work-function change is −440 meV in perfect agreement with recent measurements.[16]

Figure 2 shows a series of spectra of the LEED fine structure recorded at $\theta_i = 85°$ and for various hydrogen exposures. It is observed that the sharpness, the intensity, and the position of the fringes are modified by hydrogen chemisorption. This phenomenon never observed before may be explained by a modification of the SPB or by a change of the substrate scattering properties as hydrogen adsorbs. To clarify this point, theoretical profiles calculated with Eq. (1) are also presented in Fig. 2. An excellent fit is obtained at all coverages using a classical image barrier. Shift of the peaks are totally explained by a gradual change in the coupling parameter R. This result strongly suggests that hydrogen adsorption on W(110) does not change importantly the shape of the SPB but causes small change in the scattering propreties of this surface. Similar shifts are observed at all angles above $\theta_i = 65°$. At saturation coverage, the fine-structure fringes still obey a two-dimensional free-electron dispersion relationship.

Although the lack of resolution of their apparatus keeps them from observing changes in the fringes position, Jennings and co-workers have observed fine-structure enhancements caused by oxygen adsorption on copper single crystals.[10,11] This phenomenon is attributed to an ordered oxygen chemisorption in an interstitial site.[11] In such a situation the chemisorbed atoms would reduce the lateral variation of the SPB and thus render one-dimensional models more appropriate. On the other hand, disordered chemisorption would increase diffuse scattering and lead to the damping of the LEED fine structure. It is interesting to look at how this interpretation fits in with the observations reported here. No hydrogen-induced structure has been observed on W(110) by LEED at 300 K,[17] although a p-(1×2) pattern has been observed at all coverages by reflection high-energy electron diffraction.[18] On the other hand, besides the fact that a high-resolution energy-loss study[19] initially located chemisorbed hydrogen in an "on top" site, more recent data favor chemisorption on deeper bridge[20] or threefold coordinate hollow sites.[21] It is obvious that the present knowledge of the hydrogen W(110) system does not disregard interstitial ordered chemisorption, and we conclude that our observation is concistent with Jennings's interpretation.

In summary, a new LEED fine structure on W(110) has been observed. The results obtained indicate that an interference process rather than a resonance scattering is responsible for this feature. The modification of LEED fine structure with adsorption of gas has been demonstrated. Hydrogen chemisorption is found to affect the scattering properties of W(110) but not its SPB. Our observation supports the model of fine-structure enhancement by ordered chemisorption in interstitial sites and provide new experimental data that could help for the understanding of the chemisorption mechanism of hydrogen on W(110).

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