Reconstructive Phase Transitions and Effective Adsorbate-Adsorbate Interactions: H/Mo(100) and H/W(100)

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Low-energy electron-diffraction and infrared-absorption measurements of H/Mo(100) and H/W(100) surfaces show that, at low hydrogen coverages, the effective H-H interactions are very different for the two substrates, leading to island formation on Mo(100) and to a uniform H layer on W(100). The results can be explained by a phonon-mediated interaction mechanism for the hydrogen adatoms, according to which the difference in behavior is due to the difference in the coupling between substrate distortions induced by the individual adatoms. It is concluded that a realistic treatment of the adatom interactions should go beyond the rigid-substrate model and include the crucial role of soft surface phonons.

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The nature of the forces between atoms adsorbed on a surface is one of the central issues in surface science. The effective adatom-adatom (A-A) interactions determine the two-dimensional (2D) structure of the overlayer, regulate the dynamics of surface diffusion, and strongly influence the rates of adsorption and desorption. However, with a few notable exceptions,[1] little direct experimental information has been obtained about the origin of these interactions. Theoretical considerations of the A-A forces have included both direct interactions, such as van der Waals, dipole-dipole and orbital overlap effects, and indirect interactions mediated by the electrons or phonons of the substrate.[2-5] In this Letter we consider the effective interactions between hydrogen (H) atoms adsorbed on the (100) surfaces of molybdenum and tungsten. We have obtained experimental evidence that, despite the expected similarity of these two substrates, the effective A-A interactions are very different: At low coverage they lead to the formation of islands on Mo(100) but to a uniform layer on W(100). This surprising difference can be accounted for by a substrate-mediated interaction mechanism in which softening of substrate phonons plays an important role.

The new data obtained in the present study consist of LEED observations of 2D long-range order, showing the absence or presence of "islands," combined with infrared (ir) absorption spectroscopy, characterizing the H bonding and local substrate geometry. ir measurements at very low coverages for these weak dipoles make it possible to infer detailed information on the influence of long-range interactions on the adatom bonding.

The reconstruction of clean Mo(100)[6,7] is modified by H adsorption to give a complex phase diagram containing coexisting phases and incommensurate structures.[8] The present focus is on the structures induced at low coverage θ, because the phase diagram in this region most clearly reveals the nature of the A-A interactions. Figure 1(a) shows the clean LEED pattern at low temperature, T, due to the incommensurate (I) $c(2\times2)$ structure characteristic of the reconstructed surface. It reverts to a (1×1) structure [Fig. 1(c)] when the crystal temperature is above ≈ 220 K. This behavior is similar to that of the clean W(100) surface which shows a $c(2\times2)$ reconstructed phase below room temperature, but only a (1×1) periodicity at elevated temperatures.[6,9]

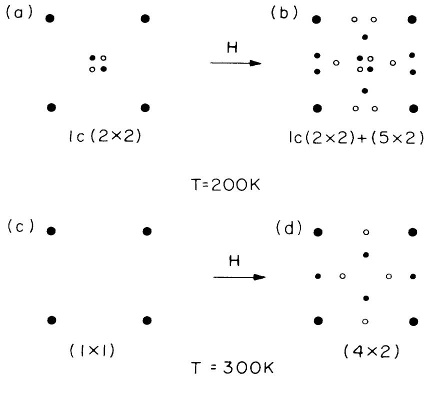

FIG. 1. Schematic representation of observed LEED patterns. (a) Incommensurate $c(2\times2)$ structure on clean Mo(100) at low T due to two domains (filled and open circles) rotated 90 degrees from each other. (b) Composite pattern observed at low T for $0<\theta<0.1$; it is due to two domains (filled and open circles) of the (5×2) structure together with the $Ic(2\times2)$ structure. (c) (1×1) structure on clean Mo(100) at high T. (d) Composite pattern at high T for $0<\theta<0.6$; it is due to two domains (filled and open circles) of the (4×2) structure.

Low-coverage [$\theta \leq 0.1$ monolayer (ML) where 1 ML corresponds to 1 H per Mo surface atom] adsorption of H_2 on Mo(100) at temperatures below 220 K produces the LEED pattern shown in Fig. 1(b). In addition to the quartet of beams present for the clean substrate [Fig. 1(a)], the pattern contains spots in $\frac{1}{5}$-order positions. With increasing H coverage the quartet of beams gradually disappears, while the $\frac{1}{5}$-order beams become stronger and reach maximum intensity at $\theta \cong 0.1$ ML. The relevant portion of the phase diagram is shown in Fig. 2. At higher temperatures ($T > 250$ K), low-coverage adsorption of H yields new beams at $\frac{1}{4}$-order positions [Fig. 1(b)] which can be assigned to a (4×2) structure.[8,10] As substantiated by the evidence presented below, at low coverages H forms islands surrounded by a sparsely covered Mo surface for both high and low temperatures.

In order to investigate the local geometry, we have measured the Mo-H vibrational frequencies throughout the coverage range 0.02 to 2 ML and over the temperature range 80 to 350 K. Some of the absorptions pertinent to the present study are shown in Figs. 3(a)-3(c). Characteristic frequencies were recorded for each of the observed surface phases, ranging from ≈ 1270 cm^{-1} at low coverage to ≈ 1000 cm^{-1} at high coverage (≤ 2 ML). For the saturated phase (2 ML) two absorptions are present; in addition to the broad line at 1020 cm^{-1}, a sharp asymmetric feature at 1300 cm^{-1} also appears. On the basis of an analysis similar to that performed for H/W(100),[11] we conclude that the H atoms in the saturated phase occupy all bridge sites of an unreconstructed substrate; i.e., 2 H per surface Mo atom. The broad line (1020 cm^{-1}) is assigned to the symmetric stretch mode (ν_1) and the asymmetric Fano line (1300 cm^{-1}) to the overtone of the wag mode ($2\nu_2$) of the Mo—H—Mo structure.[11] As is the case for H/W(100), this overtone is detected only at or near saturation coverage and disappears as soon as substrate reconstruction is observed.[11] In particular, the $2\nu_2$ mode is absent for the phases shown in Fig. 2.

The difference in absorption frequency between the various surface phases is too small to be due to a conversion from bridge site to on-top or fourfold-site adsorption. We assign the higher-frequency band (> 1020 cm^{-1}) observed at low coverage to vibrations of H on a shorter bridge site which exists on the reconstructed Mo surface. In particular, the (5×2) structure is characterized by a single absorption line at 1220 cm^{-1} [Fig. 3(b)] which is assigned to the ν_1 mode of H on a short bridge site. Over the temperature range where the (5×2) beams are observed, the ir spectrum displays no frequency shift with coverage [Fig. 3(d)] and the line remains relatively sharp (FWHM ≤ 30 cm^{-1}). Similarly, the (4×2) phase is characterized by an absorption line at

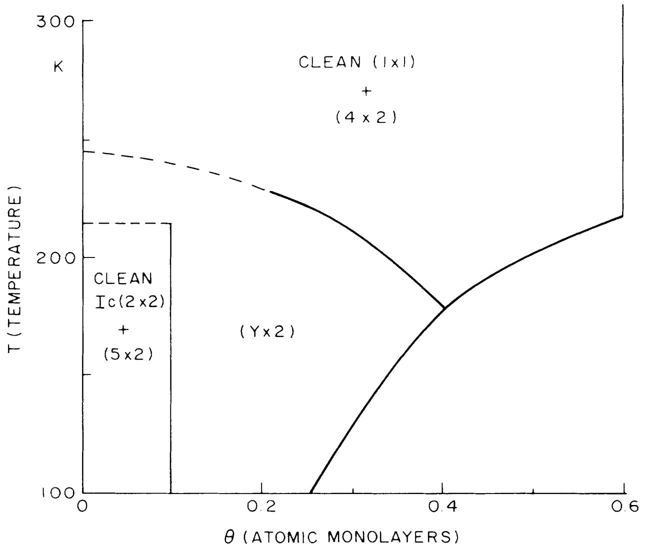

FIG. 2. Low-coverage part of the H/Mo(100) phase diagram in the T-θ plane. Broken lines indicate boundaries that are not accurately determined because of the low intensity of the extra LEED beams. In the (Y×2) region, where Y changes continuously from 5 to 4 with increasing coverage, the Mo_2H ν_1 mode displays a continuous shift from 1220 to 1210 cm^{-1}. The complete phase diagram is described elsewhere (Ref. 8).

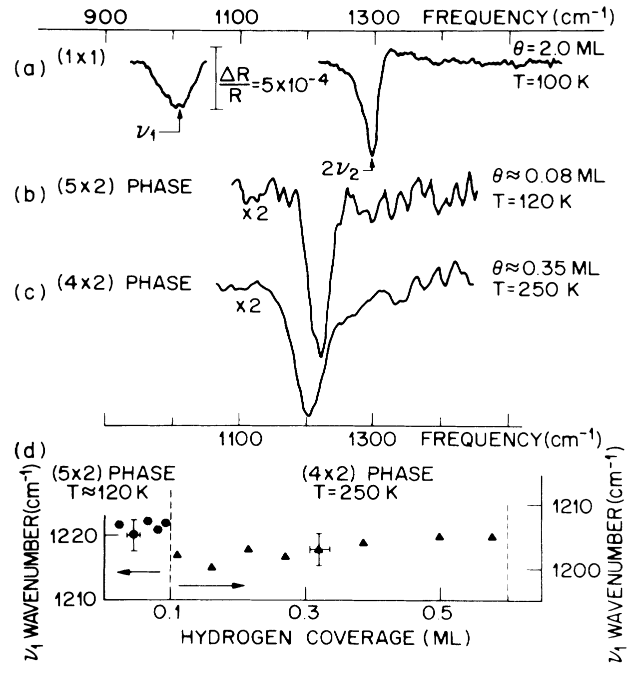

FIG. 3. ir-absorption reflection spectra associated with (a) the saturation phase, (b) the low-T, low-θ phase [Fig. 1(b)], and (c) the high-T, low-θ phase [Fig. 1(d)]. The resolution is 4 cm^{-1} for (a) and 8 cm^{-1} for (b) and (c). The plot (d) gives the coverage dependence of the center frequencies obtained by a least-squares fit of the data for a Lorentzian line shape and by a subsequent averaging over several scans in the case of the (5×2) phase.

1205 cm^{-1} [Fig. 3(c)] with negligible frequency shift in that region of the phase diagram [Fig. 3(d)]. This behavior should be contrasted to the ir data on H/W(100) which shows a large (≥ 35 cm^{-1}), continuous shift in the ν_1 mode frequency as the initial H-induced $c(2\times2)$ phase is developed ($0.04 \leq \theta \leq 0.3$).[12]

Further analysis of the LEED pattern of Fig. 1(b) indicates that the surface must consist of islands of the (5×2) structure coexisting with regions of a nearly bare reconstructed Mo(100) surface. This conclusion cannot be reached by consideration of the position of the beams in the pattern, since the same pattern would result from a single homogeneous structure with two superimposed distortion waves. These two waves would correspond to the $Ic(2\times2)$ and the (5×2) periodicities, respectively. However, measurements of the intensities of the diffracted beams show that the $Ic(2\times2)$ LEED pattern of clean Mo(100) has two perpendicular mirror lines in the [11] and $[1\bar{1}]$ directions. This remains true when the additional beams assigned to the (5×2) structure are present. On the other hand, the diffracted beams from the latter pattern always have mirror lines along the [10] and [01] directions. At least in a kinematical analysis, this implies that the Mo-atom displacements that produce the $Ic(2\times2)$ periodicity must be parallel to the [11] (or $[1\bar{1}]$) direction and those giving the (5×2) periodicity must be parallel to the [10] (or [01]) direction. Since it is impossible for a uniform structure to satisfy both of these requirements, we conclude that the surface producing the LEED pattern in Fig. 1(c) consists of coexisting $Ic(2\times2)$ and (5×2) phases. Thus, the H-induced structure is present as islands of local coverage 0.1 ML on a nearly clean Mo substrate. This conclusion is supported by the absence of a frequency shift of the ν_1 mode in that phase.

The H-induced (4×2) structure observed at higher temperature, above the $Ic(2\times2)\rightarrow(1\times1)$ transition of the clean substrate (see Fig. 2), also appears to grow in as islands. This is evidenced by the presence of weak but sharp $\frac{1}{4}$-order beams already at very low hydrogen coverage, which then steadily increase in intensity with increasing coverage. The alternative explanation, that the surface is homogeneous, requires the Mo displacements to be small initially and later to increase gradually with θ. This possibility is ruled out by the absence of a significant frequency shift of the ν_1 mode, as shown in Fig. 3(d). As is indicated in Fig. 2, the local coverage in the (4×2) islands is approximately 0.5 ML.

In contrast, the H/W(100) surface is homogeneous under these conditions. At room temperature, adsorption of hydrogen causes the rearrangement of the W atoms in the clean (1×1) phase, resulting in a uniform $c(2\times2)$ structure. The continuous variations of the W-atom displacements within this phase are manifested by a continuous and substantial shift in frequency of the ν_1 mode as θ increases. This is opposite to the ir observations on the H/Mo(100) system, summarized in Figs. 3(b)-3(d) for both high and low temperatures. Furthermore, oxygen coadsorption experiments indicate that hydrogen becomes increasingly compressed as additional oxygen is adsorbed[8,13]; this is consistent with a homogeneous H layer at low coverage ($\theta > 0.3$).

The most likely origin of the different behavior of hydrogen on W(100) and Mo(100) is through the difference in the substrate-mediated interaction which arises from the coupling between substrate distortions induced by individual adatoms. The Fourier transform of the resultant interaction $J(\mathbf{q})$ is proportional to the susceptibility $\chi(\mathbf{q})$ of the substrate which characterizes its response to a disturbance of wave vector $\mathbf{q}$.[4,14] This substrate-mediated interaction can be of appreciable magnitude when the surface has near instabilities. In that situation, the phonon modes are relatively soft at some wave vector $\mathbf{q}_0$ leading to a large value of the susceptibility $\chi(\mathbf{q}_0)$. This in turn leads to a large and negative value for the Fourier components of the effective adsorbate interaction $J(\mathbf{q}_0)$. The interaction in real space $J(\mathbf{r})$, however, could be either attractive or repulsive according to the relation

$$J(\mathbf{q}_0)=\textstyle\sum_{\mathbf{r}} J(\mathbf{r})e^{i\mathbf{q}_0\cdot\mathbf{r}}.$$

We suggest that the phonons of the clean Mo(100) surface are relatively soft at $\mathbf{q}_0=(2\pi/a)(\frac{1}{5},\frac{1}{2})$ at low temperatures and $\mathbf{q}_0=(2\pi/a)(\frac{1}{4},\frac{1}{2})$ at high temperatures (and other equivalent wave vectors in the "star" of $\mathbf{q}_0$). By contrast, the W(100) surface has only an instability at $q_0=(2\pi/a)(\frac{1}{2},\frac{1}{2})$. The phase factors $\exp(i\mathbf{q}_0\cdot\mathbf{r})$ in $J(\mathbf{q}_0)$ are such that for W(100) with $\mathbf{q}_0=(\pi/a,\pi/a)$, a strong nearest-neighbor repulsion is sufficient to render $J(\mathbf{q}_0)$ negative. In the case of Mo(100), with $\mathbf{q}_0$ at $(\pi/a,\pi/2a)$ $[(\pi/2a,\pi/a)]$ or $(\pi/a,2\pi/5a)$ $[(2\pi/5a,\pi/a)]$, the real-space interaction must have some stronger long-range attraction as part of its components to render $J(\mathbf{q}_0)$ negative.

As a consequence of the long-range attractive component in the A-A interaction, at low temperature there is a single minimum in the free energy of the H/Mo(100) system at low coverage corresponding to the $Ic(2\times2)$ phase and a single minimum at higher coverage corresponding to the (5×2) phase. In the intermediate-coverage region, there does not exist a free-energy minimum associated with a uniform hydrogen coverage phase. Thus, as the coverage is varied, a first-order transition from the $Ic(2\times2)$ phase to the (5×2) phase occurs with the system entering a coexistence region at intermediate coverages. This region consists of islands of hydrogen in a (5×2) phase and a surrounding $Ic(2\times2)$ phase of almost bare Mo(100) surface. At higher temperatures, the transition between the (4×2) and (1×1) phases corresponds to an order-disorder transition in the overlayer lattice gas. According to the Landau rules,[15] this should be a first-order transition. This is consistent with the presence of attractive components in the substrate-mediated interactions. So the free-energy behavior is similar to the low-temperature situation except that the two minima in the free energy now correspond to the (1×1) phase at low coverage and the (4×2) phase at high coverage. For W(100), the instability occurs only at $q=(2\pi/a)(\frac{1}{2},\frac{1}{2})$. This wave vector corresponds to a $c(2\times2)$ periodicity of the substrate lattice, or equivalently, a $p(2\times1)$ or a $p(2\times2)$ periodicity in the overlayer lattice comprising all the bridge sites. A second-order transition is now allowed by the Landau rules,[15] which is consistent with the presence of strong nearest-neighbor H-H repulsions.[14,16] This leads to an enhancement of the reconstruction of the W(100) surface from the (1×1) phase to the $c(2\times2)$ phase. Theoretical studies based on this picture have shown indeed that in this case the (1×1)-to-$c(2\times2)$ phase transition is second order with no H-island formation,[17] in agreement with the experimental observation.

In summary, for H/Mo(100) the H atoms tend to collect into islands. The small local density of these islands, in the low-temperature phase, indicates an effective long-range attraction combined with a repulsion at shorter range. In contrast, for H/W(100), the H atoms are dispersed and the A-A interactions are predominantly repulsive. We suggest that the very different behavior of the H-H interactions on these substrates can be understood in terms of the elastic response of the substrate. Despite the similarities in geometry and electronic structure of Mo(100) and W(100), there appear to exist differences in the surface-phonon spectra, especially with respect to the existence of soft phonons or near instabilities. This leads to a different substrate-mediated interaction on the two substrates. The detailed spectra required for the quantitative application of these ideas are not yet available. However, a test of the proposed adatom interaction mechanism should become possible when the first-principles total-energy and phonon calculations for W(100)[18-20] are extended to Mo(100) and when experimental He scattering studies[21] have been made for both surfaces.

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