Electron-stimulated ordering of adsorbed films

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(Submitted 18 June 1983)
Pis'ma Zh. Eksp. Teor. Fiz. **38**, No. 4, 162–164 (25 August 1983)

A partial electron-stimulated ordering in freshly adsorbed hydrogen films on the (011)Mo face has been detected by low-energy electron diffraction. The films were adsorbed at $T = 5$ K and were not brought to equilibrium by annealing.

PACS numbers: 61.55.Dc, 61.14.Hg, 68.45. – v

Bombardment with low-energy electrons has been observed to cause disorder in submonolayer films of light elements (H, D, and Li) at temperatures below the threshold for the appearance of a significant thermal mobility.[1–3] The effect was inferred from the decay of the features in the pattern of low-energy electron diffraction (LEED). In experiments with Li films, additional features in the diffraction pattern

 0021-3640/83/160189-04$01.00

fade completely when the films are exposed a sufficiently long time to an electron beam, but in the cases of H and D the intensities of the features in the pattern decrease only partially for certain lattices, demonstrating that a competing ordering process is occurring. In an effort to identify this process we have studied the effect of low-energy electrons on H films adsorbed on the (011)Mo surface. Judging from the results of Ref. 4, a preliminary annealing is not required in order to produce a chemisorbed atomic phase, in contrast with the case in adsorption on (001)W. Furthermore, in the case of molybdenum the effect of the bombardment by the low-energy electrons can be seen not only in an adsorbed film, which has been ordered beforehand by annealing, but also in nonequilibrium film adsorbed at a low temperature.

The procedure used in the present experiments differs from that of Refs. 1–3 in that the experiments were carried out not in a glass apparatus but in a Riber metal apparatus, modified to allow the samples to be cooled with liquid helium. The concentration of H atoms in the adsorbed film was estimated from an analysis of the adsorption kinetics and of the thermal-desorption spectra. These spectra consist of two phases: β_2 and β_1, which at saturation contain 7×10^{14} and 14×10^{14} atoms/cm^2, respectively[5]; the corresponding degrees of surface coverage are $\varphi = 1/2$ and 1.

At $T = 5$ K the films which have been brought to equilibrium (by annealing for 10 s at 300 K) exhibit a single LEED pattern with additional features characteristic of a (2×2) structure. Comparison of the changes in the intensities of these additional features during a progressive increase in the adsorption dose, on the one hand, with the changes in the thermal-desorption spectrum, on the other, showed that the filling of the β_2 state corresponds to maximum development of the ordered (2×2) structure, while the filling of the state β_1 corresponds to a transition to a (1×1) structure. Of the several possible types of film lattice which would produce the same LEED pattern (2×2), the lattice shown in Fig. 1 has the appropriate value $\varphi = 1/2$. The arrangement of adsorbed atoms in the elementary cell corresponds to the interpretation that these atoms are bound to the substrate by the orbitals of surface Mo atoms, and these orbitals make an angle of 45° with the normal (e_g orbitals). Figure 2 shows the change in the intensity of the (2×2) features during bombardment of a film with $\varphi\approx1/2$ by electrons with $E = 7.5$ eV at a current density $i = 3\times10^{-4}$ A/cm^2. The fact that the intensity does drop all the way to zero corresponds to a partial disordering of the film caused by the low-energy electrons, as has been observed previously[1,2] for the $p(2\times1)$ structure of H and D on (011)W.

For freshly adsorbed films, by which we mean films adsorbed in the absence of an

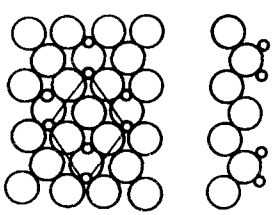

FIG. 1. Model of the H(2×2)–Mo(011) structure. Small circles—adsorbed atoms; large circles—substrate atoms.

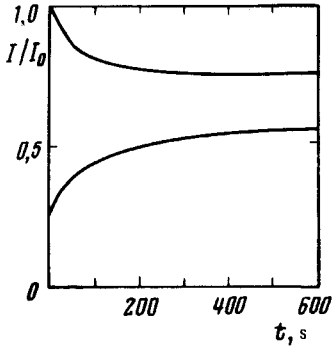

FIG. 2. Change in the intensity of the (2×2) features in the diffraction pattern of low-energy electrons during the exposure of a film to an electron beam. $\varphi = 1/2$, $E = 7.5$ eV, $i \approx 3 \times 10^{-4}$ A/cm^2.

electron beam at $T = 5$ K, without a subsequent annealing, we again see a LEED pattern with features corresponding to a (2×2) structure when the electron beam is applied. This pattern is similar to that of the annealed films, but the additional features are far fainter. As the duration of the exposure to the beam is increased, the intensity of these features increases, approaching but not actually reaching the same level as during the electron-stimulated disordering (Fig. 2). This fact, combined with the equality of the time constants for the intensity rise and decay (Fig. 2), indicates that the reason for the change in the LEED intensity induced by the electron bombardment is the same for the freshly adsorbed films and the annealed films. In one case, the process in question causes a partial ordering of an orginally disordered structure, while in the other it causes a partial disordering of a structure which was originally completely ordered. The process in question may be the migration of nonequilibrium long-lived vibrational excitations of the adsorbed hydrogen atoms[6] induced by the electron beam. This conclusion also agrees with the presence of a nonzero initial order in the freshly adsorbed film, since an energy sufficient for exciting vibrations of adsorbed atoms is liberated in each adsorption event.

The (2×2) structure exists over the entire interval $\varphi < 1$, initially (at $\varphi < 1/2$) at equilibrium with the lattice gas of adsorbed atoms and later (at $1/2 < \varphi < 1$) at equilibrium with a (1×1) structure. Curves similar to those in Fig. 2 for $\varphi = 1/2$ were obtained at other adsorption doses of L. Figure 3 shows some typical intensities I_0 of the features in the diffraction pattern of the ordered (2×2) structure found from these curves for various of L (these intensities were found at $T = 5$ K for the annealed film). Also shown here at the relative intensities I/I_0 for the following states of the film: freshly adsorbed and after prolonged exposure ($\sim 10^3$ s) of freshly adsorbed and annealed films to an electron beam. The quantity $(/I_0)(dI/dt)$ shown in this figure is the initial rate of change of the intensity induced by the beam, divided by I_0. In the first stage of the adsorption (at $\varphi < 1/2$, to the left of maxI_0), the β_2 phase with the (2×2) structure evidently grows through a first-order phase transition. The characteristic parameters of the effect of the electrons on the structure, shown in Fig. 3, remain the same. In the second state ($\varphi > 1/2$) these parameters change in a complicated way,

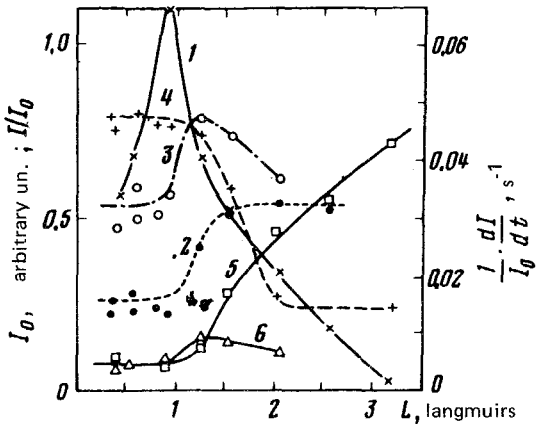

FIG. 3. Effect of the adsorption dose L on various properties. 1—Intensity of the (2×2) features in the diffraction pattern of low-energy electrons for an annealed film; 2—the intensity level I/I_0 for a freshly adsorbed film before exposure to the beam; 3—the same, after exposure to the beam; 4—intensity I/I_0 for an annealed film after exposure to the beam; 5—rate of electron-stimulated disordering; 6—rate of electron-stimulated ordering.

apparently because of an interaction between excited components of the β_1 and β_2 phases.

In the absence of the electron beam at $T = 5$ K we do not observe (over a time of several hours) an ordering in the freshly adsorbed film above the level shown by curve 2 in Fig. 3. This fact is evidence that no significant quantum ordering (tunneling) occurs under these conditions. The electron-stimulated ordering of chemisorbed atomic oxygen on (011)Mo observed in this study suggests that in $Hp(2\times1)$ — W(011) films[2] this process, rather than the quantum mobility, is responsible for the incomplete electron-stimulated disordering.

We thank O. M. Braun for a useful discussion.

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Translated by Dave Parsons
Edited by S. J. Amoretty