Two-dimensional lattices of adsorbed hydrogen on the (011) face of tungsten and their disordering

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The structure of hydrogen films on the (011) face of tungsten and the order–disorder phase transitions in these films were investigated. Disordering of two-dimensional hydrogen lattices was observed when electrons landed on the surface with thermal velocities.

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Adsorption of hydrogen on metals is of great interest both in connection with problems of surface and catalysis physics[1] and in connection with the problem of metallic hydrogen.[2] We have investigated the structure and the ordering and disordering processes of submonolayer hydrogen films on the (011) face of a tungsten crystal. This face has the "smoothest" potential relief and should favor, in principle, the appearance of possible quantum effects accompanying the adsorption of hydrogen.

The structure of the two-dimensional films was investigated by the method of slow-electron diffraction with the aid of an electronograph in which the asamples were cooled with liquid helium.[3]

The changes of the diffraction pattern, illustrated in Figs. 1(a), (b) (c), (d) were observed when the degree of hydrogen coating was increased. Contributing to the effect is the formation of the ordered structures $p(2\times 1)$, (2×2), and $p(1\times 1)$ at coating degrees[1)] θ amounting to 1/2, 3/4, and 1, respectively. The difraction patterns *a*, *b*, *c*, and *d* with the sharpest reflections were observed after annealing the film (at $T_{\text{ann}} = 30$–160 K, depending on θ). However, even without annealing, films adsorbed on the surface of a sample cooled to $T \approx 5$ K are not amorphous. Under these conditions, a certain short-range order is established in the film, and can be assessed from the electron diffraction patterns with the diffuse reflections, of the type shown in the Fig. 1(b) for $\theta = 1/2$. One of the probable causes of this phenomenon is the local change, induced by the absorption, of the potential relief of the substrate.[3]

In addition to the irreversible structure changes due to the annealing, reversible order–disorder phase transitions can be observed in the already annealed films. The parameter sensitive to the degree of order is the intensity of the superstructure reflections in diffraction. Figure 2 shows the temperature dependences of the intensity of the intrinsic reflections of the structures $p(2\times 1)$ and (2×2). They differ noticeably from the curves described by the Ising model (see, e.g., Ref. 4). The higher critical transition temperature for the (2×2) structure, corresponding to the phase β_1 observed in experiments on thermodesorption, characterizes the stronger interaction between the adsorbed atoms in this phase compared with the phase β_2, which has the structure $p(2\times 1)$.

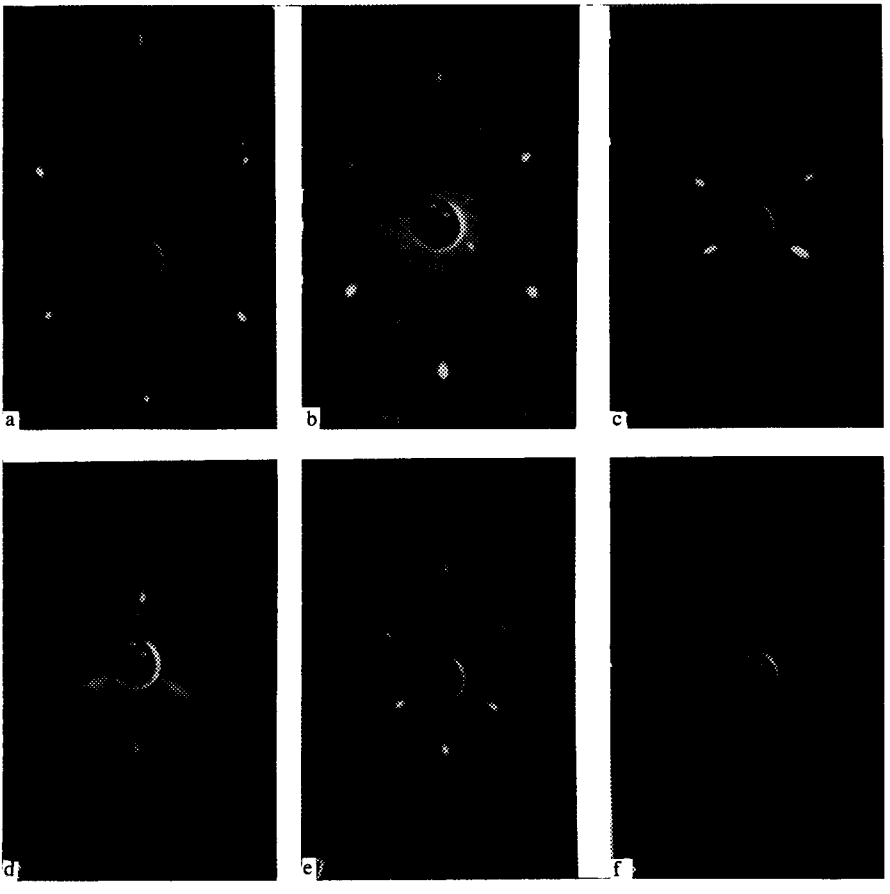

FIG. 1. Diffraction patterns of the H_2—W (011) system at $T = 5$ K: a—clean substrate (electron energy 54 eV); b—$\theta = 1/2$ after annealing at $T = 120$ K (64 eV); c—the same picture at an energy 21.4 eV; d—$\theta = 1/2$ without annealing (22.1 eV); e—$\theta = 3/4$ after annealing at $T = 160$ K (18.8 eV); f—$\theta = 23/4$ after a two-minute exposure to an electron beam (22.1 eV at a current density 5×10^{-4} A/cm^2).

At sufficiently low temperature, the two-dimensional lattices of the adsorbed atoms of hydrogen become disordered because electrons land on the surface. This manifests itself in a gradual extinction of the superstructure reflections on the diffraction pattern [(Fig. 1(f)], in a manner similar to that described earlier for the Li—W (011) system.[5] In contrast to the previously described effect, however, there was no threshold whatever observed for the electrons that destroy the surface structures of the hydrogen on the (011) surface of tungsten. The energy dependence of the rate of electron-stimulated disordering is illustrated in Fig. 3, which shows also the delay curve of the electron current from the electronograph gun. As is clear from a comparison of these plots, in this case the disorder is induced by electrons with thermal velocities. A noticeable effect of damping of the superstructure reflections (several percent per minute) can be registered when the crystal is exposed to a beam with a

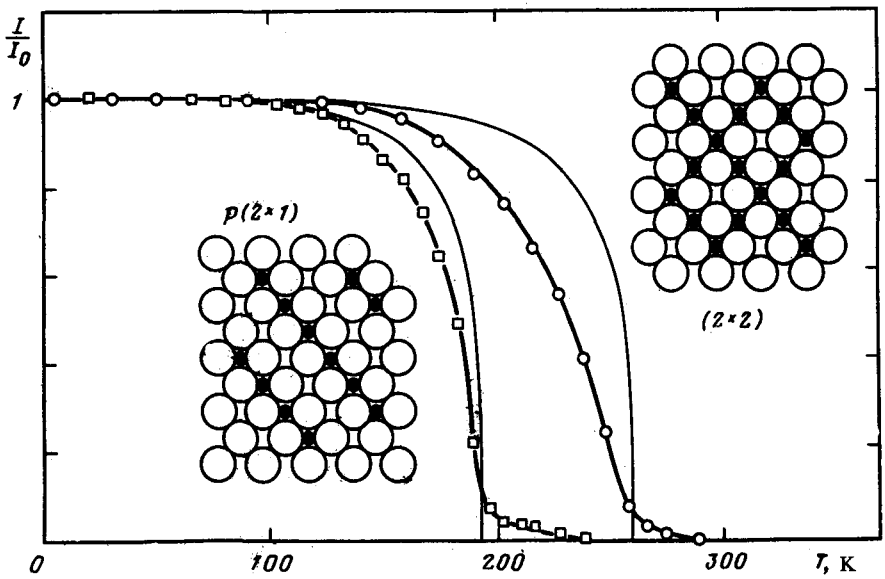

FIG. 2. Temperature dependences of the intensities of the diffraction reflections for the structures $p(2\times1)$ and (2×2). Hypothetical models of the structures are shown alongside the corresponding curves (light circles—tungsten atoms, dark—hydrogen atoms). The intensity is normalized to the value at $T = 5$ K. The thin lines show the curves for the Ising model.

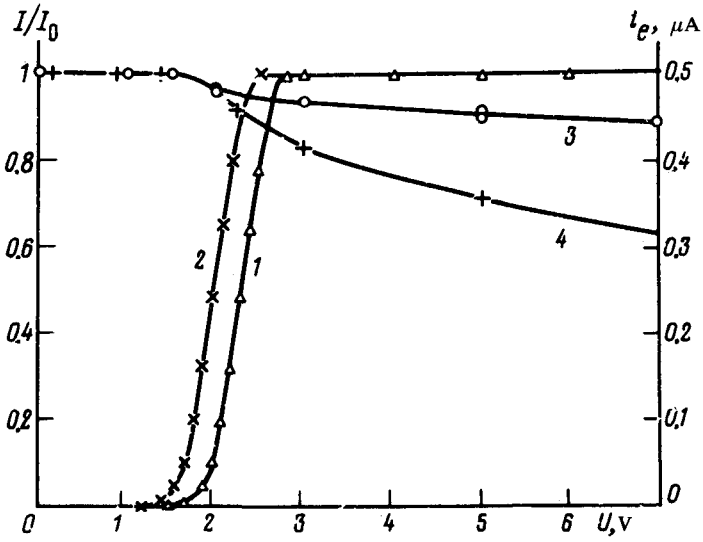

FIG. 3. Current—voltage characteristics of the electron current i_e to the crystal (1,2), and the ratio of the intensity of the superstructure reflections after a one-minute bombardment by the beam to the initial intensity (3,4) as functions of the voltage between the gun cathode and the sample. Curves 1, 3—for $p(2\times1)$ structure; 2, 4—for (2×2).

current as low as 5×10^{-8} A and with electron energies corresponding to the Maxwellian "tail" on the delay section of the current–voltage characteristic (saturation current 5×10^{-7} A, beam diameter 1 mm). It appears that the defects in the two-dimensional lattice can be produced even by extremely slow electrons on account of the energy that they release when they strike the surface. We recall that the work function of the (011) face of tungsten coated with a film of hydrogen is 5 eV. It is probable, just as in the case of electron-stimulated desorption, that an adsorbed atom interacting with an electron incident on the surface goes over into a certain metastable excited state. By excitation we mean here any possible transition from the ground state of the absorbed atom, including capture or loss of an electron, etc. The excitation is followed by a shift of the adsorbed atom to a new equilibrium position, and thus part of the energy of the electron subsystem can be transferred to the atomic subsystem. As a result, a defect can be produced in the two-dimensional lattice.

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[1)]By degree of coating we mean here the ratio of the atomic concentrations of the adsorbate to the surface atoms of the substrate. The degree of coating was determined from the data on the structure analysis of the surface.

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