Disordering of lithium films adsorbed on the (011) face of tungsten crystals irradiated by slow electrons

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It is found that submonolayer lithium films adsorbed on the (011) face of a tungsten crystal are disordered on bombardment of the surface by slow electrons. The phenomenon is of a nonthermal nature and is characterized by a threshold energy of 54 eV. It is suggested that electron impact creates a vacancy in the *K* shell of the lithium adatom, and the adatom-substrate system, in accordance with the Franck–Condon principle, undergoes a vertical transition to the potential curve of the excited state. On moving along this curve the adatom may acquire an energy sufficient for formation of a defect in the ordered two-dimensional lattice of the adatoms.

It is well known that irradiation of adsorbed gas films by slow electrons (with energy $E \lesssim 100$ eV) can produce various surface reactions—desorption, dissociation, and change of the film structure.[1] At the same time in adsorption systems of the metal-on-metal type such reactions have not been observed up to the present time. This was explained by the fact that in the latter case the binding of the adsorbed atom (adatom) with the substrate is accomplished by delocalized electrons, and therefore the excitations created in the adatoms by the incident electrons relax too rapidly for any regrouping of particles to occur on the surface.[2,3]

However, in the present work, as the result of the performance of experiments at sufficiently low temperatures, we have been able to observe in a metal-on-metal adsorbed film (lithium on tungsten) one of the effects of the type discussed—disordering of the film under the influence of slow-electron bombardment.

The structure of lithium films adsorbed on the (011) face of tungsten was studied by us by the LEED method with the substrate crystal cooled with liquid helium.[4] In addition, measurements were made of the work function by the contact potential difference method.

A similar investigation of this system was carried out earlier at room temperature.[5] Cooling of the crystal permitted observation of a number of two-dimensional structures formed by lithium adatoms, which turn out to be disordered already at $T = 300°K$. These are lattices of the type (2×3), $c(2 \times 2)$, and $c(3 \times 1)$, which correspond to degrees of covering θ equal to $1/6$, $1/4$, and $1/3$. Since the structure of a closely packed monolayer film of lithium accurately follows the structure of the (011) face of tungsten, the degree of covering is defined here as $\theta = n/n_W$, where n is the lithium adatom concentration and $n_W = 1.4 \times 10^{15}$ cm^{-2} is the concentration of surface atoms of tungsten on the (011) face. We note that the lattices of all three of these types and the electron diffraction patterns corresponding to them have already been described in detail,[6] since they have been observed also in adsorption of sodium on the (011) face of tungsten.

In the work with a cooled crystal ($T = 5$ K) it was observed that the intensity of the fractional (superstructure) reflections corresponding to the lithium-adatom lattice decreases rapidly during observation of the diffraction pattern if the primary electron-beam energy exceeds a threshold value 54 ± 1 eV. Figures 1 and 2 show typical electron-diffraction patterns and the time dependence of the intensity of the fractional reflections illustrating this effect. Figure 3 shows the rate of decrease of the intensity of the reflections for three different structures as a function of the beam energy, which indicate that the phenomenon has a clearly expressed threshold nature. We note that in obtaining these data the results of the irradiation were always recorded under standard conditions: the crystal was held under a beam of a given energy for a certain time and then the beam energy was reduced to 26 eV, at which the attenuation of the reflections is no longer observed, and under these conditions the intensities were measured.

Measurements of the work function showed that it is essentially unchanged during the irradiation. Therefore the attenuation of the superstructure reflections cannot be due to desorption of the lithium film, which strongly reduces the work function of the substrate. Thus, the irradiation effect reduces to destruction of the long-range order in the adsorbed lithium film. It should be noted, however, that the short-range order in location of the adatoms is preserved in this case, as indicated by the existence of characteristic halos in the electron-diffraction pattern.

A number of facts indicate that the disordering of the film under electron bombardment is not an ordinary thermal disordering due to local heating of the sample under the action of the beam. In fact, if the disordering were thermal, then by gradually reducing the beam energy it would be possible to observe a restoration of the long-range order. However, ordering of the structure

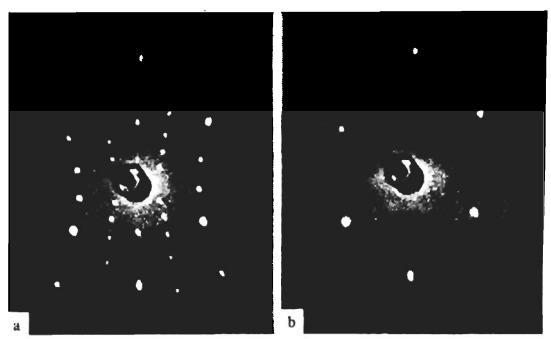

FIG. 1. Electron-diffraction patterns of the system Li-W (011): a—directly after annealing of film, (2 X 3) structure; b—disappearance of superstructure reflections after electron bombardment of the surface. E = 55 eV, current density $j \approx 5 \times 10^{-4}$ A/cm^2, t = 13 min, T = 5 K.

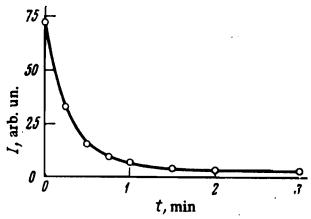

FIG. 2. Time dependence of the intensity of reflections of the (2 X 3) structure during electron bombardment of the surface. E = 80 eV, T = 5 K.

destroyed by the bombardment can be achieved experimentally only by annealing the film at a temperature at which the adatoms of lithium become sufficiently mobile (35—100 K). Also in disagreement with the hypothesis of thermal disordering is the fact that the threshold energy turns out to be identical for three structures with greatly differing disordering temperatures (100, 110, and 235 K respectively for structures with $\theta = 1/6$, $1/4$, and $1/3$). Thus, electron-stimulated disordering has a specific, nonthermal nature.

On the basis of data on the rate of attenuation of the reflections $I_0^{-1}dI/dt$ (I_0 is the intensity at the time t = 0) and on the current density in the beam ($j \approx 5 \times 10^{-4}$ A/cm^2), it is possible to estimate the cross section σ for the ejection of an adatom from its normal location corresponding to an ordered structure. If n_n is the concentration of adatoms in normal locations, then directly after turning on the beam we have

$$-dn_n = \sigma n_n e^{-1} j dt,$$

where e is the electronic charge. Since the intensity of the super-structure reflections is proportional to the square of the long-range-order parameter,[7] it is easy to show that in the initial part of the bombardment when the destruction of the long-range order is still small,

$$\frac{dn_n}{n_n} \approx \frac{1-\theta}{2}\frac{dI}{I_0}.$$

Hence

$$\sigma = \frac{1-\theta}{2}\frac{e}{jI_0}\left|\frac{dI}{dt}\right|.$$

The function $\sigma(E)$ calculated by means of this expression on the basis of the curves of the rate of attenuation of the reflections are shown in Fig. 3 by the dashed lines. From the data obtained it follows that the values of σ in the energy range investigated reach $\sim 10^{-17}$ cm^2. The values of σ are lower, the higher the density of the adsorbed film, so that for $\theta \geq 2/3$ we were already unable to observe any appreciable effect of the electron beam on the film structure. Apparently the main factor producing a decrease in σ with increase of θ is the increase in the interaction energy of the adatoms with each other and the related increase in the energy for formation of defects in the film. We note that for the same reason the order-disorder phase-transition temperature also increases with increasing θ and for $\theta \to 1$ reaches ≈ 500 K.

The results presented permit us only to engage in preliminary discussions of the physical nature of the electron-stimulated disordering process. We note first of all that the energy which can be transferred by an electron to an adatom in an elastic collision is in our case $\sim 10^{-3}$ eV. It is too small for a defect in the film to be formed as a result. In fact, judging from the temperature at which annealing of the defects occurs, the activation energy of the annealing process amounts to $\sim 10^{-2}$—10^{-1} eV, and the energy necessary for producing a defect cannot be less than this value.

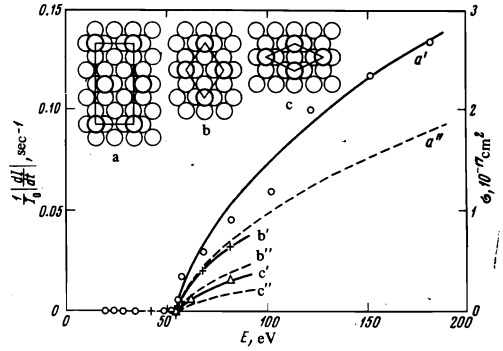

FIG. 3. Models a, b, and c—unit cells of the structures (2 X 3), c(2 X 2), and c(3 X 1) of lithium atoms on W (011); a', b', c'—dependence of initial rate of falloff of intensity I of reflections of structures a, b, and c on beam energy (left scale, I_0 is the intensity at t = 0); a'', b'', c''—dependence of cross section σ for structures a, b, and c on beam energy (right scale).

We are struck by the fact that the threshold energy for electron-stimulated disordering is close to the energy $E_{KF} = 55$ eV which is necessary to transfer an electron from the K level to the Fermi level in lithium (ref. 8, p. 324). It is natural that in an adsorbed lithium atom the difference in the energies corresponding to the K level and the valence-electron level can differ somewhat from the value of E_{KF}, which refers to massive lithium. However, this difference can hardly be greater than the width of the Fermi distribution in metallic lithium,[9] which amounts to only ≈ 3 eV. Consequently, we can suggest that the first stage of the electron-stimulated disordering process is excitation of the lithium adatom—creation of a vacancy in its K shell. According to refs. 10 and 11, the cross section for this process in the lithium atom under electron impact amounts to $\sim 10^{-17}$ cm^2, so that the above suggestion is consistent with the experimentally observed values of σ.

To explain the mechanism of electron-stimulated surface reactions, Menzel and Gomer[2] and Redhead[3] have drawn on the Franck-Condon principle, in accordance with which on electron impact the adatom-substrate system performs a vertical transition from the potential curve of the ground state to the curve of the excited state. Since the minima in these curves occur at different distances of the adatom from the surface, the excited adatom will be shifted from its initial position and so can acquire a kinetic energy sufficient to overcome some activation barrier.

The most probable channel for relaxation of excitation in the lithium adatom is the Auger process with emission of an electron, the relaxation time[8] being 10^{-15}—10^{-16} sec (see chapter 2, sections 2 and 5, of ref. 8).[1)] Thus, if the mechanism considered by these authors[2,3] is realized in electron bombardment of lithium films, then as a consequence of the small value of the relaxation time of the excitation in comparison with the time of atomic processes ($\sim 10^{-13}$ sec), the kinetic energy acquired by the adatom cannot be significant. For example, it can hardly be sufficient for desorption of an adatom, which acquires an energy of the order of several electron volts. In fact, neither in our system nor in other systems investigated of the metal-on-metal type has electron-stimulated desorption been observed.[1,2] In addition, we cannot exclude the possibility that in the process discussed the adatom can acquire an energy sufficient to move it from one adsorption center to another. According to the estimates given

above, this transfer requires an activation energy $\sim 10^{-2}$–10^{-1} eV.

From the point of view discussed we can also explain why electron-stimulated disordering of strontium films on the (011) face of tungsten is not observed (this investigation was also carried out at liquid-helium temperature[4]). It is evident that as a consequence of the significantly larger mass, the strontium atom, other conditions being equal, moves during its lifetime in the excited state a smaller distance than the lithium atom. Correspondingly the kinetic energy acquired by it in moving along the potential curve of the excited state will also be smaller and, evidently, insufficient to produce a defect in the ordered structure.

It must, however, be recognized that the data existing at the present time are insufficient to consider the interpretation presented as unique. It is possible, for example, that in the electron-stimulated disordering process some role is played by relaxation of excitation of another type—in particular, surface plasmons and specific bound-electron states formed on creation of a vacancy in the inner shell of the atom or in the Auger process.[12,13]

Thus, the results of the present work show that it is not always possible to neglect the effect of slow-electron bombardment on the structure of adsorbed metal films, as has been done up to this time. Further study of the electron-stimulated disordering process apparently can provide useful additional information on the nature and characteristics of the adsorption bond.

It must be emphasized that the most important condition for observation of electron-stimulated disordering of adsorbed films of metals is cooling of the samples to sufficiently low temperature, since at high temperatures a rapid annealing of the effects occurs simultaneously with their formation. This fact, which must be taken into account also in observation of radiation defects in the volume of solid bodies,[14] is especially important in study of surface processes, which are characterized by smaller activation energies.

The authors are grateful to V. A. Ishchuk for helpful remarks.

[1)]We note that the recoil energy which the lithium atom can receive on emission of an Auger electron amounts to 4×10^{-3} eV and, as in the case of elastic scattering of the primary electrons, apparently is insufficient to produce a defect.

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126