Manifestation of phase states of a submonolayer film in surface diffusion of barium on the (001) face of molybdenum

Yu. S. Vedula, A. T. Loburets, and A. G. Naumovets

Physics Institute, Ukrainian Academy of Sciences
(Submitted 27 June 1978)
Pis'ma Zh. Eksp. Teor. Fiz. **28**, No. 4, 258–261 (20 August 1978)

Investigations of the surface diffusion of barium on the (001) face of molybdenum has revealed singularities on the diffusion distribution; these singularities correlate with the structural transitions in the submonolayer film of barium.

PACS numbers: 68.48. + f, 73.30. + y, 66.30.Jt

Adsorbed submonolayer films, which are quasi-two-dimensional systems, have in the general case rather complicated phase diagrams. Changes of the structure of the film with increasing concentration of the adsorbed atoms correlate with the changes of

 0021-3640/78/160238-04$00.60

electronic properties of the surface and the kinetic characteristics of the adsorption.[1] We report here results of experiments that demonstrate the influence of the phase state of the film on the surface-diffusion process.

We investigated the surface diffusion of barium on the (011) face of molybdenum. As shown in Ref. 2, at small degrees of coating, the barium atoms form two-dimensional lattices that are matched to the structure of the substrate (Figs. 1a and 1b). At

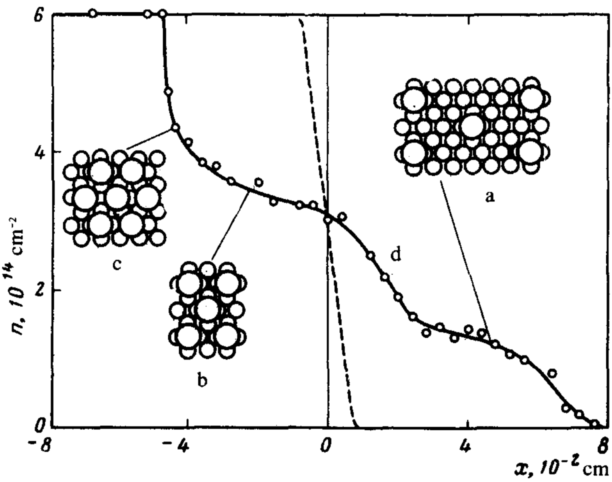

FIG. 1. a–c) Models of surface structures in accord with Ref. 2. a) With (6×2), b) with (2×2), c) hexagonal structure. Small circles—Mo atoms, large—Ba atoms. d) Distribution $n(x)$ of the Ba atoms over the substrate after heating at $T = 450$ K for 12 min. The initial distribution is shown dashed.

adsorbed-atom concentrations $n > 3.5 \times 10^{14}$ cm^{-2} the film and the substrate are no longer structurally matched—the adsorbed atoms form a two-dimensional hexagonal lattice (Fig. 1c) whose period decreases smoothly until a dense monolayer is produced at $n = 6 \times 10^{14}$ cm^{-2}.

Using a moving electron gun that produced a beam of ≈ 20 μm diameter, we measured the distribution of the work function ϕ over the surface, and then, knowing the $\phi(n)$ dependence, we determined the distribution $n(x)$ of the adsorbate on the substrate.[3]

In the course of diffusion of the barium from the initial monolayer coating, assumed to have the form of a "step," two sections are observed on the $n(x)$ curves within which the gradient $|dn/dx|$ is relatively small: at small concentrations ($n \approx 1.3 \times 10^{14}$ cm^{-2}) and at $n \approx 3.5 \times 10^{14}$ cm^{-2} (Fig. 1d). It follows therefore[4] that in the indicated coating regions, the first of which corresponds to a lattice of type with (6×2) (Fig. 1a) and the second with (2×2) (Fig. 1b), the diffusion coefficient D is enhanced. (At temperatures exceeding the temperature of the order-disorder transition for these structures, the characteristic short-range order of these transitions is apparently preserved in the films[2].)

If the initial coating consists of more than a monolayer, it is impossible to observe the diffusion of the barium by the "unrolling carpet" mechanism[5] (In this case a dense monolayer should be produced on the forward edge of the diffusion distribution and should serve as a substrate for the diffusion of the atoms in the second layer). This conclusion is illustrated by the results shown in Fig. 2. To obtain these data, a solid Ba layer ("pedestal") was first sputtered on the surface, with some concentration n_p. This was followed by additional sputtering of a coating in excess of a monolayer on part of the surface, with an abrupt boundary ("step"). Under conditions when $n_p < 3.5\times10^{14}$ cm^{-2}, the diffusion distributions always exhibit a plateau corresponding to $n=3.5\times10^{14}$ cm^{-2}, i.e., to the phase with (2×2) (Fig. 2a). We recall that the phase

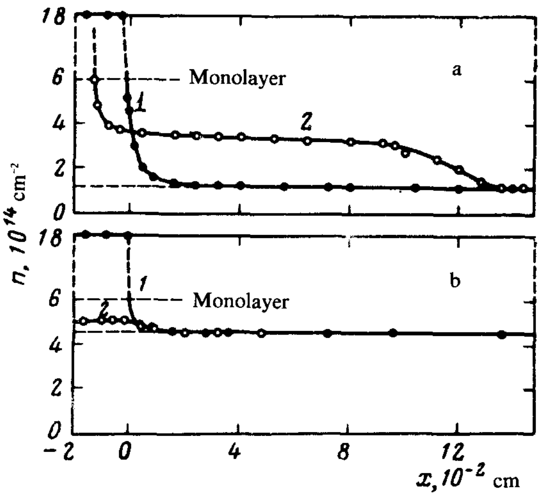

FIG. 2. Plots of $n(x)$ prior to heating (1) and after heating (1) of monolayer films: a—$n_p = 1.2\times10^{14}$ cm^{-2}, $T = 500$ K, $t = 15$ min. b—$n_p = 4.5\times10^{14}$ cm^{-2}, $T = 550$ K, $t = 55$ min. Initial coating in the "steps" consist of three monolayers. The concentrations in the "pedestal" are marked by the horizontal dashed lines.

with (2×2) has almost half the density than the total monolayer, and constitutes a two-dimensional condensate: if the concentration of the adsorbed barium atoms on the (011) face of the molybdenum is increased by sputtering from the gas phase, then after a certain critical coating is reached ($n\approx2\times10^{14}$ cm^{-2} at 77 K), a first-order phase transition of the type of two-dimensional condensation from this coating to the phase with (2×2) is observed.

When $n_p > 3.5\times10^{14}$ cm^{-2}, which corresponds to formation of a hexagonal structure, the diffusion is substantially slowed down, and the coating on the right of the "step" is also always submonolayer, while the concentration decreases smoothly with distance. In a certain sense, the "pedestal" critical coating $n_p \approx 4.5\times10^{14}$ cm^{-2} (Fig. 2b). It corresponds to a hexagonal lattice whose period in the $[0\bar{1}1]$ direction coincides with the period of the lattice of the (011) face of molybdenum (Fig. 1c). At this and larger values of n_p (including a solid monolayer coating), it is impossible at all to register diffusion by the employed method. This result can be explained in the following manner. At $n > 4.5\times10^{14}$ cm^{-2}, the value of D in the first monolayer decreases sharply, as is evidenced by the large value of the gradient $|dn/dx|$ in this region of coatings (Fig. 1d). On the other hand, the diffusion boundary is likewise not noticeably shifted by the diffusion in the second layer. It is possible that the detachment of the barium atoms from the multilayer coatings (two-dimensional sublimation) requires so large an activation energy, that at the corresponding temperature the detached atoms are very rapidly desorbed from the second layer into the vacuum. In this case they cannot diffuse over a distance that could be noticed within the limits of the resolution of the method. Attempts to accelerate the diffusion by increasing the temperature lead only to rapid evaporation of the "step" (Fig. 2b).

The foregoing results show that changes of the phase state of the submonolayer film, which occur when the concentration of the adsorbed atom increases, manifest themselves distinctly in the surface-diffusion process. We note that in Refs. 2, 3, and 6 the diffusion distributions also exhibited some singularities for submonolayer coatings, but no direct information was given concerning the structure of the films investigated in these references.

The authors thank V.K. Medvedev and A.G. Fedorus for useful discussions.

[1]L.A. Bol'shov, A.P. Napartovich, A.G. Naumovets, and A.G. Fedorus, Usp. Fiz. Nauk **122**, 125 (1977) [Sov. Phys. Usp. **20**, 432 (1977)].
[2]A.G. Fedorus, A.G. Naumovets, and Yu.S. Vedula, Phys. Status Solidi A **13**, 445 (1972).
[3]Yu.S. Vedula and A.G. Naumovets, in: Poverkhnostnaya diffuziya i rastekanie (Surface Diffusion and Flow Nauka, 1969, p. 149.
[4]S.D. Gertsriken and I.Ya. Dekhtyar, Diffuziya v metallakh i splavakh v tverdoĭ faze (Diffusion in Metals and Alloys in the Solid Phase), Fizmatgiz, 1960.
[5]I.L. Sokol'skaya, in: Poverkhnostnaya diffuziya i rastekanie (Surface Diffusion and Flow), Nauka, 1969, p. 108.
[6]R. Butz and H. Wagner, Proc. of Seventh Intern. Vacuum Congress and Third Internat. Conf. on Solid Surfaces, Vienna, 1977, p. 1289.