Spreading of a Rarefied Phase and Nonmonotonic Concentration Profiles in Surface Diffusion of Lithium on the (112) Plane of Molybdenum

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Evolution of a rarefied two-dimensional Li phase with a concentration less than 1/50 of a monolayer has been found in the process of Li surface diffusion on Mo(112). The formation of this Li phase is interpreted as evidence of the existence of very long-range lateral interactions. We have also observed a nonmonotonic shape and quite unexpected development of Li concentration profiles on Mo(112).

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Recent studies of surface diffusion of adsorbates have revealed numerous manifestations of surface phase transitions in diffusion kinetics [1]. Actually, under conditions of local equilibrium, the diffusion zone represents a display of two-dimensional adsorbate phases which are formed immediately in the course of diffusion. Each phase has its specific set of diffusion parameters determined by the substrate potential corrugation, atomic structure of the phase itself, and lateral interaction of adsorbed atoms (adatoms). This generally results in complex-shaped concentration profiles. Experimentally measured profiles $\theta(x)$ (θ is a degree of coverage and x is a coordinate directed along the diffusion flux) usually show up a number of "terraces" (slowly descending or nearly flat sections) and "steps" (sharp drops in θ). The terraces correspond to continuous transitions like, e.g., commensurate-to-incommensurate transitions, while the steps correlate with first-order transitions [1-3]. With all these peculiarities, the vast majority of $\theta(x)$ profiles observed up to now in surface diffusion exhibits one or another type of the monotonic decline of coverage ($d\theta/dx < 0$) from an initial value $\theta=\theta_0$ to $\theta=0$ [1,4]. Only quite recently in a study of Au surface diffusion on Si(111) Ichinokawa *et al.* [5] have detected an oscillatory coverage distribution corresponding to the emergence of two alternate phases in the spreading Au adlayer. However, the physical mechanism of this effect is not understood.

In this work we report on surface diffusion experiments in which nonmonotonic coverage profiles (of quite different type than those described in Ref. [5]) have been observed for Li adatoms on Mo(112). A strikingly rarefied Li phase has also been found to appear in the course of the Li diffusion on Mo(112), and a very unusual evolution of the coverage profiles has been established.

The (112) plane of molybdenum consists of parallel close-packed rows of Mo atoms separated by atomically deep furrows [Fig. 1(a)]. We applied a technique in which a narrow (≈ 20 μm) electron beam is utilized to measure the distribution of the work function over the crystal surface [1]. With the use of the calibrated dependence of the work function on lithium coverage, the work function distribution is converted into the coverage profile. In general, the work function depends not only on coverage, but also on the structural state of the adlayer. To avoid possible ambiguities connected with this fact, we have obtained the calibration curves [Fig. 1(b)] using the following procedure: (i) small equal doses of Li were sequentially deposited on the surface; (ii) after deposition of each dose, the adlayer was first annealed at the temperature of subsequent diffusion experiments and then cooled to 77 K for the work function measurements. The work function practically leveled off after the first two minutes of annealing at all operating temperatures. The attained accuracy of θ determination is estimated at $\delta\theta \approx 0.002$ [$\theta=1$ is ascribed to a lithium monolayer in which the surface concentration of Li adatoms equals that of molybdenum atoms on the (112) plane, namely, 8.3×10^{14} cm^{-2} [6]].

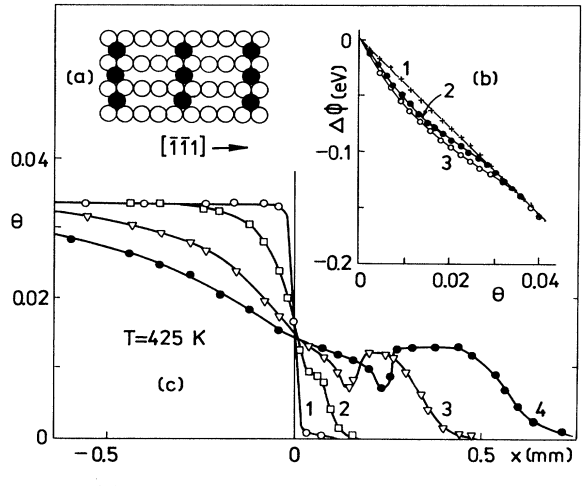

FIG. 1. (a) Structure of the Mo(112) surface (open circles; only atoms in the uppermost layer are depicted). A chain structure $p(1\times4)$ of Li ($\theta=0.25$) is shown by filled circles [6]. (b) Work function change of Mo(112) vs Li coverage ($T=77$ K): without annealing Li adlayer (1); with annealing 5 min at 425 K (2); with annealing 3 min at 500 K (3). Annealings were made after deposition of each Li dose. (c) Diffusion of Li out of a steplike initial deposit (1) on Mo(112). Annealing times ($T=425$ K) are 2 min (2), 26 min (3), and 65 min (4).

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The experiments were carried out at a residual pressure of $\sim 10^{-11}$ Torr. The molybdenum crystal and lithium evaporator were carefully outgassed. Lithium was evaporated on the crystal cooled with liquid nitrogen ($T=77$ K). Using different masks placed between the evaporator and crystal, we could set up initial coverage profiles shaped as a step, stripe, or trench. The adlayer boundary in the initial deposits was perpendicular to the atomic furrows so the surface diffusion proceeded quasi one dimensionally along the furrows [Fig. 1(a)]. To activate the diffusion, the crystal was heated up to 300-600 K. Li coverage profiles resulting from the diffusion were taken after cooling the crystal back to 77 K. In this paper we restrict ourselves to the results obtained at low lithium coverage ($\theta < 0.1$). A full version of the work will be published elsewhere.

Figure 1(c) shows the time evolution of an initial steplike coverage profile. There are two unexpected features in this diffusion process. The first is the formation of a rather extensive terrace which corresponds, depending on the observation conditions, to surprisingly low coverages within the range $0.01 < \theta < 0.02$. The second unusual feature is a concentration hollow between the terrace and the boundary of the initial profile. The depth of this concentration hollow is $\Delta\theta \leq 0.01$. The width of the trailing edge after the terrace remained approximately constant (≈ 40 μm) in all experiments. Under appropriate conditions it was possible to obtain quite wide terraces. For example, on continuous depositing of lithium upon a half of the crystal (with another half screened with a mask), we were able to grow the terrace ~ 0.7 mm wide within 3 h at $T=425$ K.

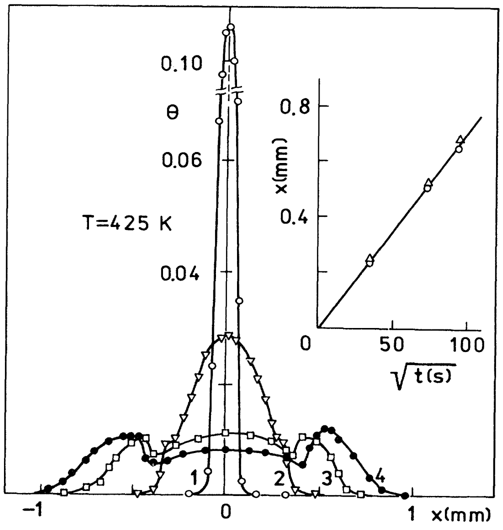

FIG. 2. Diffusion of Li out of a stripelike initial deposit (1) on Mo(112). Annealing times are 20 min (2), 90 min (3), and 150 min (4). Inset: Displacement of leading edges of the profiles (taken at $\theta=0.005$) vs square root of time (time in seconds). Open circles correspond to the right edge and triangles to the left edge of the profiles.

A similar behavior was found in the experiment where the initial Li coverage profile represented a stripe ≈ 100 μm wide (Fig. 2). The coverage nonmonotonicities were formed symmetrically on both sides of the initial distribution, and again the width of the trailing edges of the terraces was ≈ 40 μm. Slight deviations from the strict symmetry might be due to uncontrollable surface defects. As long as a Li concentration gradient existed within the region of the initial profile, the adlayer boundary and trailing edges of the terraces propagated in accordance with the diffusion law $x \propto \sqrt{t}$ (Fig. 2). The nonmonotonic features vanished after heating the crystal at elevated temperatures $T > 500$ K. However, they were restored if the heating temperature was reduced back to $T \leq 500$ K. [It should be noted that at $\theta < 0.1$ thermal desorption of Li from Mo(112) starts only at $T=700$ K [6]]. We were not able to determine the low-temperature limit of the effect. At least at $T=300$ K the formation of the coverage nonmonotonicities and terraces was still observed (in $t \sim 10$ h).

The diffusion of lithium in the case of a trenchlike initial profile is illustrated in Fig. 3. The obtained diffusion profiles were also symmetrical and again the nonmonotonic features were revealed. The diffusion of the adsorbate into the trench resulted, at some intermediate stage, in the appearance of a terrace confined with two concentration hollows. Under such conditions the coverage within the terrace is twice as high as in the above mentioned configurations and falls within the range $0.02 < \theta < 0.04$. On further heating at the same temperature or at another temperature within 300-500 K, the width of the plateau diminished until it vanished completely.

In all experiments where we managed to scan the whole diffusion zone we could verify the conservation of the amount of lithium on the surface within the accuracy of coverage determination ($\leq 10\%$).

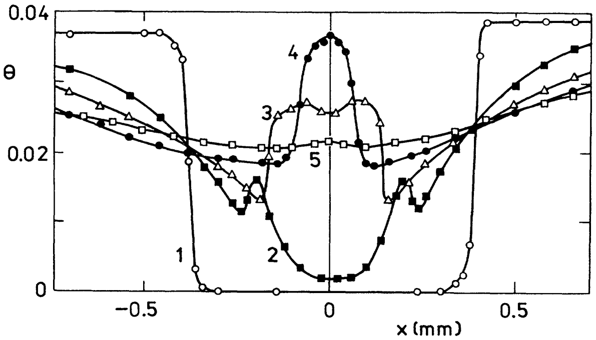

FIG. 3. Diffusion of Li out of a trenchlike initial deposit (1) on Mo(112). Annealing temperatures and times are $T=425$ K, $t=50$ min (2); $T=425$ K, $t=115$ min (3); $T=445$ K, $t > 20$ min, $T=500$ K, $t=5$ min (4); and $T=500$ K, $t=15$ min (5).

These findings raise a number of intriguing questions. The first one relates to the origin of the terraces on the concentration profiles arising in the lithium diffusion. One may surmise that they correspond to some two-dimensional Li phase with a surprisingly low concentration of the adatoms. It should be noted, however, that Gupalo *et al.* [6] who investigated the structure of Li adlayers on Mo(112) using low-energy electron diffraction (LEED) did not detect any ordered structure at $0.01 \leq \theta \leq 0.02$. Starting from $\theta \approx 0.07$ they found that the surface is covered with growing two-dimensional islands of a $p(1\times4)$ structure whose stoichiometric coverage is $\theta = 0.25$ [Fig. 1(a)]. It is questionable, however, if a standard LEED apparatus, used in [6], was sufficiently sensitive to detect such a rarefied ($\theta \leq 0.02$) and, probably, not well-ordered phase. Actually, even if the structure of this phase were isotropic, the nearest-neighbor distance in it would amount to ≈ 30 Å. In the case that adatoms coalesce into chains like those in the $p(1\times4)$ structure [Fig. 1(a)], the distance between the chains should exceed 100 Å. Up to now the largest interchain spacing, recorded for Sr on Mo(112), was 24.5 Å [7]. Li, Hock, and Palmer [8] have recently reported on observations of the submonolayer structure of potassium on graphite with periodicity ≈ 60 Å. These results suggest that the formation of a long-period phase in the Li adlayer on Mo(112) also cannot be ruled out.

The next question concerns the nature of the lateral interactions which could provide the stability of such a phase. Two major contributions to the lateral interaction which are believed to exist for alkali adsorbates on metals are the dipole-dipole repulsion and oscillating indirect (substrate-mediated) interaction [7]. The initial (at $\theta \to 0$) dipole moment of the lithium adatom on Mo(112) is 1.4 D [6]. The dipole-dipole repulsion between the adatoms decays as r^{-3} and is unlikely to produce sizable effects at $r \approx 30$ Å. By contrast, the indirect interaction should diminish as r^{-1} along the furrows on Mo(112), since there are flattened sections in the Fermi surface of Mo oriented normal to the $[\bar{1}\bar{1}1]$ axis [7]. This interaction is effectively enhanced if the adatoms are strongly bound within the chains.

It seems also relevant to consider the possibility of mesoscopic structurization in which case an adlayer consists of alternating domains differing in density. This phenomenon can be caused by surface stress and/or electrostatic interaction (the latter may be more essential if the adatoms possess a significant dipole moment) [9–11]. An example of such long-period (60–140 Å) self-organization has been found recently in oxygen adlayers on a furrowed surface Cu(110) [12]: They represent periodic arrays of stripes consisting of the coalesced oxygen chains (termed "strings" in Ref. [12]). Since our system Li/Mo(112) shows a rather strong work function variation with coverage and Li adatoms tend to form chains on Mo(112), one may speculate that the spreading dilute Li adlayer can also have some mesoscopic structure which is beyond the spatial resolution of our technique. The fact of doubling the terrace coverage in some experiments [cf. Fig. 3 with Figs. 1(c) and 2] seems to speak for domain (or island) morphology of the dilute phase.

Finally we turn to possible reasons for the unusual evolution of the concentration profiles. The peculiar character of this evolution is exhibited in the formation of the concentration hollow behind the spreading terrace. If one assumes that the Li diffusion flux **J** obeys the equation $\mathbf{J} = -L\nabla\mu$ (L being the transport coefficient and μ the chemical potential), the existence of the rising section ($d\theta/dx > 0$) in the profiles may indicate that in the course of diffusion the adlayer dynamically penetrates into the part of the phase diagram bounded by spinodal curve where $d\mu/d\theta$ is negative. This gives rise to the local uphill diffusion which can build up the stable lithium phase through a nonactivated precipitation process [13]. It is known that spinodal precipitation can produce nonmonotonic (modulated) concentration distributions whose shape depends both on the diffusivity and the interactions in a system [13]. It must be kept in mind, however, that in our case the phase transitions proceed in the presence of a directed mass transport. As can be seen from Fig. 1(c) the shape of the concentration hollow and the height of the terrace are conserved in the course of their displacement and/or spreading as long as (i) the leading edge of the terrace remains "free" (so that the growth of the terrace is unimpeded), and (ii) there is a sufficient concentration gradient within the initial deposit. However, as soon as two terraces meet in the middle of the concentration trench (Fig. 3), the process assumes a qualitatively different character. The fused terrace first heaves up to $\theta \approx 0.04$ and can even surpass in height the maximum coverage in the initial profile if this coverage is below $\theta = 0.04$ (which is conceivable in the case of an uphill diffusion). Then both peculiarities, the terrace and hollows, blur out. The reasons for such a peculiar behavior remain puzzling to us, but we are inclined to believe that an adequate description of the observed profiles could be given in terms of a nonlinear reaction-diffusion process [14,15] (the surmised phase transition in our case may be considered as a "reaction" between Li adatoms and vacant adsorption sites on the molybdenum surface).

It is pertinent to mention that Larikov *et al.* [16] have recently found the alternating regions with increased and decreased diffusate concentration in the volume diffusion of gallium in aluminum. The authors attributed this effect to the emergence of a dissipative structure.

In summary, we have presented the first observations of the spreading of very dilute phase in the course of the Li surface diffusion on the Mo(112) plane. This demonstrates the prominent role of long-range interactions in alkali metal adlayers which in our case may be additionally enhanced by the tendency of the adatoms to form strongly anisotropic (chain) structures on the furrowed surfaces like Mo(112). Thus our experiments continue a series of recent works which were performed with different techniques and detected pronounced long-range correlation effects in surface phenomena [8,12]. These results lend new impetus to further investigations of the nature of the interactions on surfaces. Such features of the diffusion as the nonmonotonic shape and highly peculiar evolution of the Li concentration profiles might reflect a nonlinear character of processes in the diffusing (strongly nonequilibrium) lithium adlayers on Mo(112).

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