
SURFACE DIFFUSION IN LITHIUM SUBMONOLAYER FILMS ON THE (112) SURFACE OF TUNGSTEN

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Making use of the method of contact potential difference, the kinetics of surface diffusion in lithium submonolayer films on the (112) surface of tungsten has been investigated. The experimental data evidence for the collective character of surface diffusion, which results in both the substantial modification of the diffusion parameters, as the surface concentration of adsorbed atoms varies, and the dynamical self-organization of the diffusion zone. The concentration dependences of the diffusion parameters of various electropositive adsorbates have been compared, and their common features and distinctions have been discussed. The influence of the electric field on the kinetics of surface diffusion has been discussed as well.

Even if we speak of the jump of a separate atom, actually, a certain number of its neighbors, with whom it interacts more or less intensively, takes part in this event. Owing to this interaction, the atom fluctuatively receives an excess energy from the substrate which serves as a heat reservoir, that is sufficient for overcoming the energy barrier. The barrier height is also defined by the interaction with neighboring atoms. After the excess energy has been returned back to the substrate, the jump of the atom comes to the end. However, under condition that there exists an ensemble of adsorbed particles (atoms or molecules) on the surface, the diffusion kinetics of each of them is governed not only by its interaction with the substrate, but also by the lateral interactions with the neighboring particles in the adsorbed film. The lateral interaction of adsorbed particles includes a number of components, with some of them possessing a long-range character [4]. All this fills the SD notion with an abundant physical content, in particular, predetermines the existence of a close interrelation between the SD kinetics and the film phase state. Neither the SD kinetics nor the kinetics of the surface phase transitions and many other surface phenomena can be realized without elucidating the regularities of this interrelation [5].

1. Introduction

The analysis of the literature shows that about 1/5 of the works published recently and dealing with the surface physics issues is devoted to the study of surface diffusion (SD) [1]. An enhanced interest to SD can be explained by the fact that this phenomenon is an indispensable and an important stage in a number of surface processes and corresponding technologies, such as growing the crystals and thin films, the deposition of coatings of various types, catalysis, sintering and powder metallurgy, wetting and spreading, friction, and so on [1, 2]. If we aim at understanding those processes at the atomic-molecular level (it is this approach that is characteristic of the surface science development nowadays), a profound comprehension of SD mechanisms at the same level is obligatory. The role of SD grows substantially if we turn to nanoscale dimensions, because the time of diffusion is known to be proportional to the mean square of the diffusive displacements of particles. So, the relevant alterations (they may be either desirable or not), realized through diffusion in nanosized objects, can run very rapidly.

An important stimulus for physicists to study the SD processes profoundly is the fact that diffusion in general is basically a collective (many-particle) phenomenon [3].

At our laboratories, a cycle of systematic researches has been carried out concerning the diffusion in the films adsorbed on the surface of tungsten and molybdenum crystals [6–11]. Both these metals possess the bcc structure, and their lattice constants differ only by 0.6%. Studying the SD of various adsorbates on their surfaces would make it possible to elucidate the role, which a number of factors may play in the SD kinetics, in particular, the chemical nature of the adsorbate and the substrate, the structures of the substrate surface and various adsorbed film phases, and the influence of lateral interactions on the SD parameters and mechanisms.

The purpose of this work was to study SD in lithium submonolayer films on the (112) surface of tungsten in

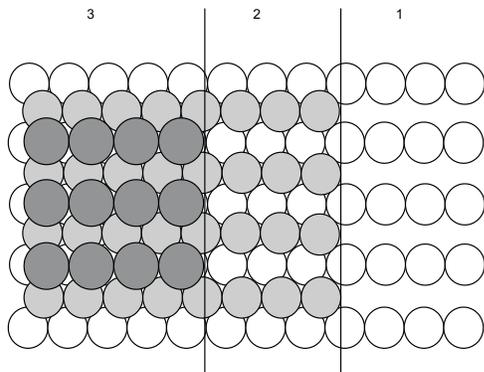


Fig. 1. Atomic structure of the (112) surface of tungsten (1) and the films of lithium on it at $\theta_{\text{Li}} = 1$ (2, a geometrical monolayer) and $\theta_{\text{Li}} = 1.9$ (3, a physical monolayer)

detail and to compare the SD parameters in this and other related systems investigated by us earlier. We have discussed the nature of the correlation between the variations of the SD parameters and the phase transitions in adsorbed films, in particular, the strong growth of the SD coefficients in the region of transition from the commensurate film structure to an incommensurate one (C-I-transition), where topological solitons may serve as mass carriers during the SD process. We have also suggested the model that can explain the influence of strong electric fields on the SD parameters of electropositive atoms. Some preliminary results obtained by us for the system Li–W(112) have been published in work [9].

One should bear in mind that the (112) surface of bcc crystals has a strongly pronounced anisotropic structure (Fig. 1). It consists of densely packed rows of atoms separated by the grooves of atomic depth (for tungsten, the groove depth amounts to 1.29 Å). It results in the strong anisotropy of diffusion: if the temperature is not too high, the coefficient of diffusion along the grooves is several orders of magnitude larger than that across the grooves, owing to which SD has practically a quasi-one-dimensional character on such surfaces [6].

2. Method

In this work, we studied lithium diffusion on the W(112) surface making use of the contact potential difference method [12, 13]. Owing to recent developments, the spatial resolution in determining the work function by this method has been improved to approximately 1 μm , so that it has got the name of scanning contact-potential

microscopy (SCPM). In order to obtain quantitative data concerning the SD kinetics, every experiment was initiated with creating the distribution of Li adatoms in the form of a concentration step, the edge of which was always oriented perpendicularly to the atomic grooves on the surface, i.e. perpendicularly to the $[\bar{1}\bar{1}1]$ direction. Then, the variations of the adatom concentration profiles in time were registered at various temperatures. To determine the concentration distribution of lithium adatoms in the diffusion zone, the SCPM method takes advantages of a change of the work function of the substrate surface, which accompanies adsorption. As a rule, the work function depends nonlinearly on the degree of surface coverage with an adsorbate. In this work, the coverage θ_{Li} is defined as the ratio between the Li adatom concentration and the concentration of W atoms on the (112) surface, i.e. $\theta_{\text{Li}} = n_{\text{Li}}/n_{\text{W}(112)}$, where $n_{\text{W}(112)} = 8.2 \times 10^{14} \text{ cm}^{-2}$. According to the terminology adopted now in the literature, the coverage $\theta_{\text{Li}} = 1$ is defined formally as a “geometrical” monolayer (ML), although, as is seen from Fig. 1, such a coverage in the case of lithium does not provide the total screening of the W(112) surface with adatoms. In this connection, the concept of a so-called *physical* monolayer, the formation of which ensures the full screening of the substrate, is introduced sometimes (Fig. 1). For the system Li–W(112), such a coverage corresponds to $\theta_{\text{Li}} \approx 1.9$ (at $\theta > 1$, i.e. when the second and the following monolayers become filled, the atomic radius of lithium is about 10% larger than that in a compressed monolayer with $\theta_{\text{Li}} = 1$, the structure of which reproduces that of the substrate [14]). The difference between the definitions of the geometrical and physical monolayers should be taken into account when interpreting the dependences of diffusion parameters on the coverage degree.

While measuring the variation of the work function using the SCPM method, one records the shift of the current-voltage characteristics of the thermoemission current onto a specimen studied, which serves as a collector (the method of retarding potential) [15]. The experimental setup and its characteristics, as well as other details of measurements, were described in works [12, 13]. The experiments were carried out under a pressure of residual gases lower than 10^{-9} Pa. Single crystals of tungsten and molybdenum, with the surface orientation (112), adsorbate evaporators, and an electron gun which formed a narrow beam of electrons for probing the surface, were placed into a glass tube. The scanning of the surface using this beam was carried out by means of the programmable rotation of a permanent magnet, between the poles of which

the experimental device (a vacuum tube) had been placed. The resolution of the determination of surface coordinates was about $1 \mu\text{m}$, and the measurement of the work function variation was carried out with an accuracy of not worse than 0.001 eV .

In order to recalculate the measured distributions of local values of the work function $\varphi(x)$ into the concentration diffusion profiles $\theta_{\text{Li}}(x)$, where x is the coordinate reckoned along the atomic grooves, we used the calibration curve $\varphi(\theta_{\text{Li}})$, which reflected the dependence of the work function on the W(112) surface on the coverage (Fig. 2). This dependence had been measured experimentally beforehand. The first minimum of the work function upon the lithium adsorption was achieved at $\theta_{\text{Li}} = 0.75$. It is known that the appearance of the work function minimum is due to the progressive depolarization of adatoms owing to their lateral interaction. Within the coverage interval $0 < \theta_{\text{Li}} < 1$, lithium fills the grooves on the tungsten surface. The emergence of the work function minimum evidences for the beginning of the metallization process within the rows of lithium adatoms that aligned along the grooves. At $\theta_{\text{Li}} = 1$, lithium adatoms occupy the grooves densely, being placed in them at a distance of 2.74 \AA from one another. It is a *geometrical* monolayer of lithium with the $p(1 \times 1)$ structure, which is imposed on the film by the substrate, and its formation correlates with the appearance of the first maximum in the curve $\varphi(\theta_{\text{Li}})$. In this case, however, the rows of lithium adatoms are separated by tungsten atoms in the $[1\bar{1}0]$ direction (across the grooves), because the nearest distance between the grooves is equal to 4.47 \AA . This allows lithium adatoms to form bonds not only with lithium adatoms in the first monolayer while building the second geometrical monolayer, but also with tungsten atoms. Therefore, lithium adatoms in the second monolayer are also strongly polarized, which manifests itself in a substantial variation of the work function in the course of filling this monolayer and in the formation of a rather deep second minimum in the dependence $\varphi(\theta_{\text{Li}})$. The completion of building of the second lithium monolayer is marked by the appearance of another maximum of the work function, which was close by its value to the work function of bulk lithium. Thus, the dependence $\varphi(\theta_{\text{Li}})$ for lithium adsorption on the W(112) surface has well-pronounced features connected to the assembling of the first and the second monolayer. They are convenient to be used when determining the lithium concentration and plotting the concentration profiles in diffusion experiments. In so doing, the accuracy of evaluating θ_{Li} in the regions, where the work function changes

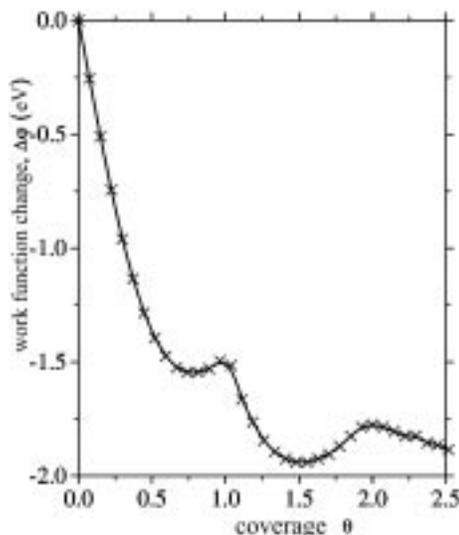


Fig. 2. Dependence of the variation of the work function at the (112) surface of tungsten on the degree of its coverage with lithium at room temperature

substantially ($\theta_{\text{Li}} \leq 0.5$), is equal to 10^{-3} ML, and approximately to 10^{-2} ML in the regions with $\theta_{\text{Li}} > 0.5$.

The initial step-like profile of the lithium concentration was created by the vacuum deposition of lithium atoms produced by an evaporator through a relevant mask. In various experimental setups, lithium was evaporated onto either a clean W(112) surface or a W(112) surface that had been preliminary covered with a uniform layer of lithium with a certain predetermined coverage degree. The concentration profiles of lithium obtained after diffusion at various temperatures and durations of the crystal annealing, were used for the calculation of the diffusion coefficients by a version, proposed in work [7], of the Boltzmann–Matano method [16,17]. The values of all diffusion parameters quoted below were obtained for diffusion in the $[\bar{1}\bar{1}1]$ direction, i.e. along the atomic grooves on the W(112) surface. In addition, all presented results concern the experiments where diffusion had the so-called normal character. This means that the mean square displacements of points on the diffusion profiles which correspond to various constant concentrations of lithium, $\theta_{\text{Li}} = \text{const}$, grow proportionally to the diffusion time: $x^2 \propto t$.

3. Experimental Results

Fig. 3 displays an example of the concentration profile recorded upon SD of lithium on the W(112) surface. The

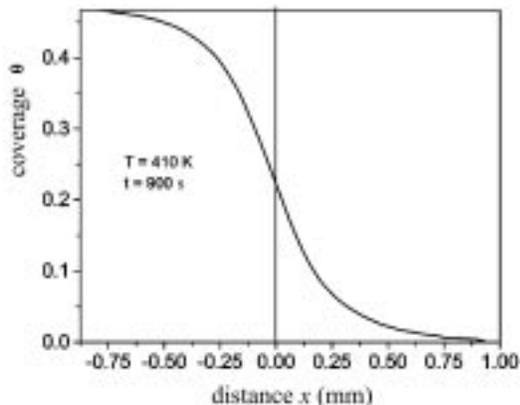


Fig. 3. Concentration profile $\theta_{Li}(x)$ at diffusion of lithium on the (112) surface of tungsten. The edge of the initial profile is located at $x = 0$

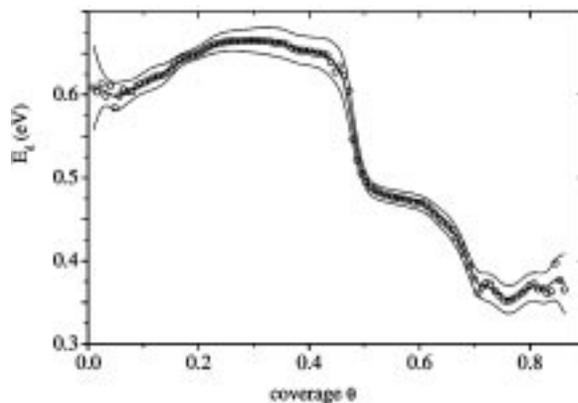


Fig. 6. Concentration dependences of the activation energy of diffusion E_d for lithium on W(112). The thin lines mark the spread limits for calculated results

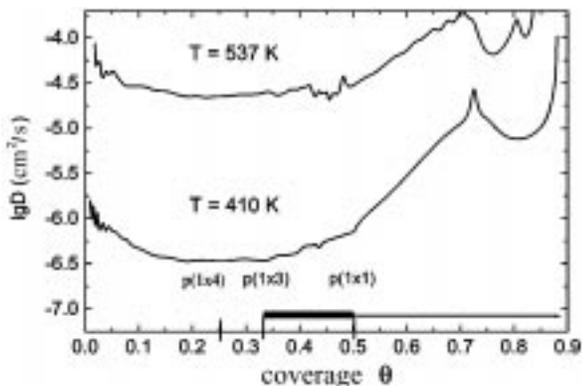


Fig. 4. Concentration dependences of the diffusion coefficient of lithium $D(\theta_{Li})$ on the (112) surface of tungsten. The thick line at the bottom shows the PT-I region, the thin line with an arrow the region of incommensurate structures

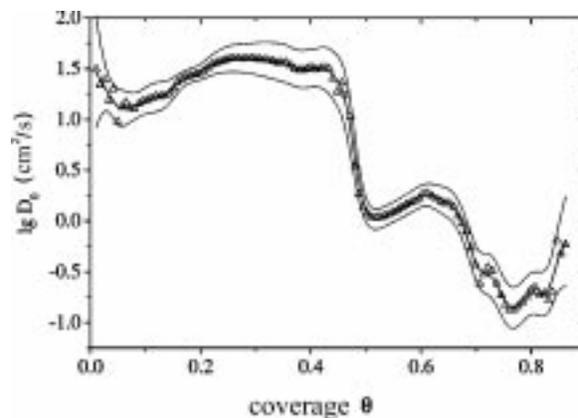


Fig. 7. Dependences of the pre-exponential factor D_0 in the Arrhenius equation on the concentration for diffusion of lithium on W(112). Thin lines show the spread limits of the results of calculations

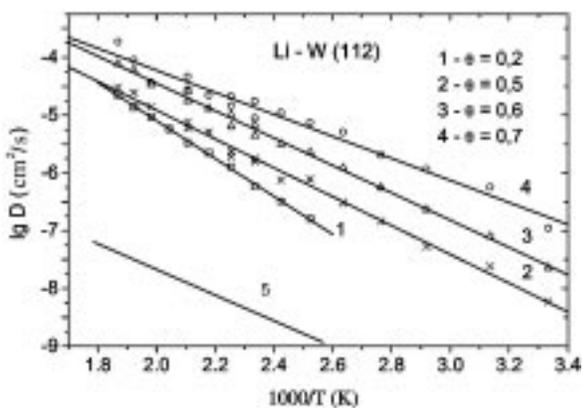


Fig. 5. Arrhenius plots for the diffusion coefficient of lithium on W(112) for various coverages θ_{Li} (1-4) and the same plot for $\theta_{Li} = 0.6$ on W(112) from work [34] (5)

coverage dependence $D(\theta_{Li})$ of the diffusion coefficient of lithium calculated on its basis is shown in Fig. 4 (the bottom curve). Fig. 4 also exhibits a low-temperature cross-section of the phase diagram of the adsorption system Li-W(112) [4, 14]. The comparison of the dependence $D(\theta_{Li})$ with the phase diagram evidences for the existence of correlation between the SD parameters and the film structure. This correlation will be discussed below. The dependences $D(\theta_{Li})$ obtained at various temperatures are used for plotting the Arrhenius plots (Fig. 5) and calculating the concentration dependences of both the diffusion activation energy E_d (Fig. 6) and the pre-exponential factor D_0 (Fig. 7). The activation energy of diffusion E_d in the first lithium monolayer ($\theta_{Li} < 1$) increases at first as the coverage grows, being

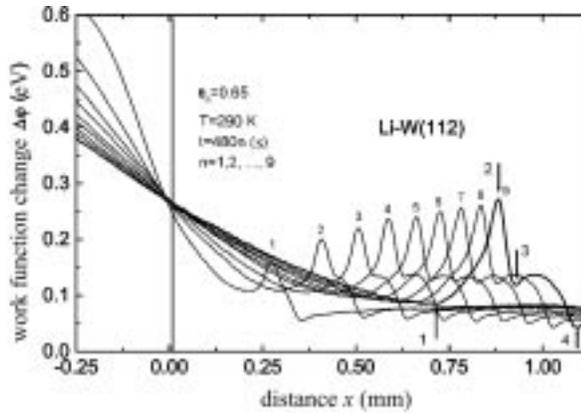


Fig. 8. Evolution of the profiles of variations of the work function for diffusion of lithium on the W(112) surface preliminarily covered with a homogeneous layer of lithium with $\theta_b \approx 0.65$. The edge of the initial concentration step ($\theta_{Li} \approx 1.3$) was located at $x = 0$

close to 0.67 eV within the interval $0.2 < \theta_{Li} < 0.45$. In a rather narrow interval of concentration $0.45 < \theta_{Li} < 0.5$, an abrupt reduction of E_d down to 0.47 eV is observed. Afterwards, within the interval $0.5 < \theta_{Li} < 0.6$, the value of E_d changes weakly. One more reduction to the value $E_d \approx 0.35$ eV occurs at $\theta_{Li} > 0.6$. The behavior of the pre-exponential factor D_0 is similar to that, i.e. the so-called compensation effect is observed. Within the limits of the first monolayer, the value of $\lg D_0$ changes in the range from -1 to $+1.6$ (D_0 is quoted in terms of cm^2/s units).

In order to study the phase character of diffusion in a Li film on the W(112) in more detail, the entire $3 \times 8\text{-mm}^2$ surface of the crystal was covered with a uniform lithium film (a “pedestal”) corresponding to $\theta_{Li} \approx 0.65$. Afterwards, this film was covered additionally with a concentration “step” of lithium with the total coverage $\theta_{Li} \approx 1.3$ and the edge perpendicular to the $[\bar{1}11]$ direction, i.e. to the direction of grooves. Fig. 8 exhibits the diffusion-induced evolution of the distribution $\varphi(x)$ of local values of the work function that were registered in this experiment. The consecutive distributions $\varphi(x)$ were recorded every 480 s. We present the original data of measurements, without recalculating the value of the work function into the coverage value. It has been done for the reason that under the conditions of this specific experiment, the work function turns out dependent (within the limits of about 0.1 eV) not only on the coverage but also on the temperature of the crystal and, probably, on structural changes in the adsorbed film of lithium. Therefore, under the circumstances, the recalculation of the work function into the coverage

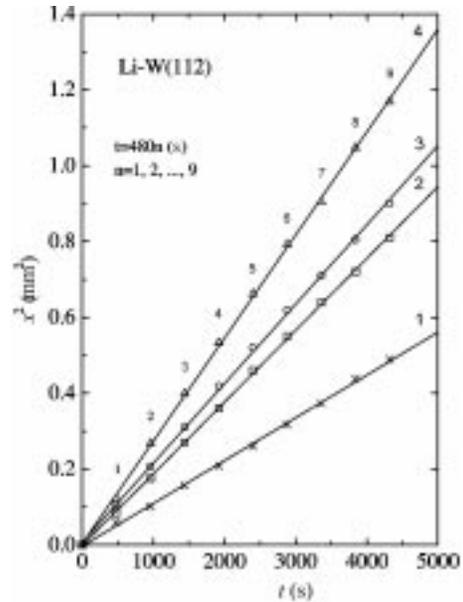


Fig. 9. Time-evolution of the extremum position in the $\varphi(x)$ profiles. The symbols are numbered according to the sequence of profiles. The figures near the straight lines correspond to the numbers of extrema in Fig. 8

value cannot be regarded as sufficiently exact. Nevertheless, information concerning the diffusion kinetics can be extracted even from the original profiles $\varphi(x)$. For this purpose, it is possible to take advantage of the availability of the extrema in the dependences $\varphi(x)$ (they are marked by the numbered arrows in one of the curves in Fig. 8) if one makes the natural assumption that there is a correspondence of those extrema with certain structural states (phases) of the adsorbed film and the coverage values (see Fig. 2). Thus, it follows from Fig. 8 that, under the experimental conditions described above, the mobility of lithium adatoms along the grooves is very high even at room temperature ($D \sim 10^{-6} \text{ cm}^2/\text{s}$). The displacements of the extrema of the $\varphi(x)$ profiles in time are shown in Fig. 9 in the (x^2, t) coordinates. The linear character of those dependences testifies to that the process of surface diffusion of lithium adatoms has a “normal” character within the chosen concentration interval. It should be emphasized that the diffusion zone, some part of which is depicted in Fig. 8, ranges over more than 2.5 mm, being therefore enormous in the atomic scale ($\sim 10^7$ lattice constants of tungsten). Nevertheless, even at such distances of diffusion, the evolution of the $\varphi(x)$ profiles runs rather regularly, and those profiles do not manifest any significant local nonhomogeneities that could be connected with large surface defects. This testifies to

that the surface structure of the tungsten crystal under investigation is rather perfect (within the resolution limits of the SCPM method).

The rapid evolution of concentration profiles caused by high values of the diffusion coefficients was observed in the second lithium monolayer even at temperatures lower than 300 K.

4. Discussion of Results

4.1. Dependences of the diffusion parameters on the structure of the lithium adlayer on the $W(112)$ surface

In order to interpret reasonably the obtained dependences of D , E_d , and D_0 on the coverage value (Figs. 4, 6, and 7), it is important to confront them with the phase diagram of the adsorbed film of lithium. One should bear in mind that, at low coverages ($\theta_{\text{Li}} \leq 0.5$), lithium atoms on the (112) surfaces of tungsten and molybdenum form chain structures, similarly to what strontium adatoms do on these surfaces [4]. The atomic chains are aligned perpendicularly to the grooves. An increase of the lithium adatom concentration on the $W(112)$ surface within the interval $0 < \theta_{\text{Li}} < 0.5$ is accompanied by the consecutive formation of the structures $p(1 \times 4)$, $p(1 \times 3)$, and $p(1 \times 2)$ [14]. In so doing, within the range $0.33 < \theta_{\text{Li}} < 0.5$, the phases $p(1 \times 3)$ and $p(1 \times 2)$ coexist, i.e. there occurs a phase transition of the first order (PT-I). The further growth of the coverage is accompanied by the formation of structures in the lithium film which are incommensurate (incoherent in one dimension) with the substrate and transform into the $p(1 \times 1)$ structure when approaching the full monolayer ($\theta_{\text{Li}} \rightarrow 1$).

The diffusion coefficients tend to growing at extremely low coverages ($\theta \rightarrow 0$), where the manifestations of the lateral interaction are minimal. However, it should be taken into account that the influence of surface defects such as various traps which can inhibit the adatom mobility and, correspondingly, reduce the diffusion coefficients has to be maximal under those conditions.

As is seen from Fig. 4, the broad minimum in the dependence $D(\theta_{\text{Li}})$ for the system Li- $W(112)$ correlates with the PT-I region, i.e. with an inhomogeneous state of the lithium film, with the diffusion coefficient becoming lower even when one approaches the PT-I region from the side of low coverages. It may be connected with the formation of nuclei of the more dense phase $p(1 \times 2)$. Under the circumstances, the diffusion

process will include the stage of atom detachment from the nuclei or larger islands of the dense phase, i.e., in fact, the stage of two-dimensional evaporation [18]. Atomic clusters can also play the role of mass carriers. In this case, the clusters would constitute, most probably, some chain segments. It is obvious, in general, that if the film is heterogeneous, its various areas (phases) should be characterized by different diffusion coefficients. Therefore, the diffusion coefficient, which would be determined under those conditions with the help of macroscopical methods (including the SCPM one), would be a certain effective value [2]. Moreover, the large gradient of concentration at the interface of two phases questions the eligibility of applying the linear approximation when considering diffusion in the PT-I region [19]. Thus, this problem requires a separate theoretical analysis, in particular, making allowance for mechanical stresses that arise around the islands [20], the influence of defects on the distribution of nuclei [21, 22], the features of percolation in the diffusion zone [23], and so on. Anyway, the effective value of the diffusion coefficient, calculated in this work from experimentally registered concentration profiles by the Boltzmann–Matano method, has a minimum in the PT-I region.

On the contrary, the diffusion coefficient grows rapidly in the concentration range $0.5 < \theta_{\text{Li}} < 0.75$, which corresponds to the phase transition of the second order (PT-II) from the commensurate structure of the film to an incommensurate one (here, the incommensurability of the film and substrate structures is meant). One should bear in mind that a similar behavior is typical of a number of other systems as well [6, 7, 9, 11, 24]. It can be explained assuming that diffusion is governed, under the conditions of the PT-II transition, by the soliton mechanism, the essence of which is illustrated in Fig. 10. There occurs a diffusive shift of incommensurate domain walls, which can be described as topological solitons [25–27], in the commensurate phase. In the case concerned, the soliton is a linear object. Solitons in adsorbed films were observed experimentally (see, e.g., [28, 29]). A soliton can move not as a whole at one jump, but by forming a pair kink–antikink with their following motions in opposite directions [30–32]. As a result, a progressively longer section of the soliton becomes shifted by the period of a substrate lattice. Of course, all those motions are stochastic, so that both separate kinks and the soliton as a whole execute random walks. Actually, solitons “meander” fluctuatively and, provided the gradient of concentration, transfer mass according to diffusion laws. There is a lateral interaction between solitons, as well

as between separate adatoms, which affects the gradient of the chemical potential. Calculations show that the activation energy of soliton jumps, owing to their essentially collective mechanism, can be much lower than the activation energy for individual adatoms [25]. Our experimental results (Fig. 6) testify to that the activation energy reduces from 0.60 to 0.35 eV, i.e. by a factor of 1.7, at the transition from $\theta_{\text{Li}} \rightarrow 0$ to $\theta_{\text{Li}} = 0.75$. Generally speaking, the theory that would explain the non-monotonous variation of the diffusion coefficient at the C-I-transition has not been developed yet. At a qualitative level, it is clear that as the solitons commence to overlap in a dense film, the film becomes totally incommensurate, and its modulus of elasticity should grow; therefore, both the parameters and the mechanism of diffusion should change substantially.

The correlations between the phase transitions in the film and the features of the dependences $E_d(\theta_{\text{Li}})$ and $D_0(\theta_{\text{Li}})$ are also observed (Figs. 6 and 7). However, the variations of these diffusion parameters are opposite to the variations of $D(\theta_{\text{Li}})$. In particular, the maxima rather than the minima of these parameters correspond to the PT-I region, while in the region of the phase transition from the commensurate structure to an incommensurate one (the PT-II region), the quantities E_d and D_0 generally diminish. We note that the value of D_0 varies by three orders of magnitude. In our opinion, several factors might be responsible for such considerable variations. First, not only may the energy E_d change substantially as a result of the coverage variation induced by lateral interactions but also the entropy of diffusion activation ΔS (the exponent $\exp(\Delta S/k)$ enters into the factor D_0 [19]). Secondly, the factor D_0 is proportional to the square λ^2 of the length of diffusion jumps, whereas this parameter can differ essentially in films of different densities [2, 33]. At last, it should be noted that the very application of the Arrhenius equation for treating the diffusion data can be not quite justified; it is especially true in the region of phase transitions. The point is that not only may the probability of the overcoming of a constant barrier change, as was supposed in the Arrhenius approximation [1–3], but also the system itself (e.g., its order parameter or the potential relief, owing to the substrate reconstruction).

We note, e.g., that the maximum of the diffusion coefficient of lithium in the region of the C-I-transition is more pronounced at lower temperatures. This follows from the comparison of the dependences $D(\theta_{\text{Li}})$ measured at $T = 537$ and 410 K [9] (Fig. 4). For the systems Sr–W(112) and Sr–Mo(112), we obtained the

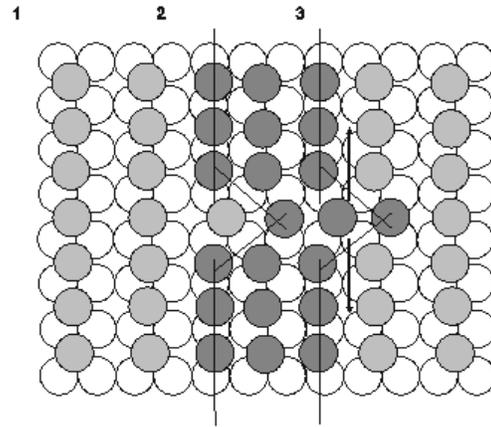


Fig. 10. The model of a soliton (a domain wall) with kinks in the film with the structure $p(1 \times 2)$: commensurate $p(1 \times 2)$ domains (1 and 3) and a soliton (2)

Arrhenius plots with breaks [7]. However, from the standpoint of what has been said, it should be realized that even if such plots could be regarded as linear with a good approximation (concerning the factors D , they are experimentally determined in a rather narrow interval of temperatures), the parameters E_d and D_0 calculated from them would represent some effective quantities. We note that all diffusion experiments dealing with lithium on the W(112) surface were carried out at $T \geq 300$ K, i.e. in the temperature range where, according to the data of work [14], the long-range order in the films is essentially violated, but the short-range one is still kept.

Despite the difficulties concerning the exact definition of diffusion parameters, it is beyond doubt that the SD rate considerably depends on the coverage and the structure of adsorbed phases. This results in the dynamic (nonequilibrium) self-organization of the diffusion zone, owing to which the phase possessing the highest diffusion coefficient occupies the largest area in this zone [5, 9, 24].

4.2. Comparison of Li, Sr, and Dy diffusion characteristics on W(112) and Mo(112)

For a better understanding of the results presented above, it is expedient to compare them with the results of researches of other electropositive adsorbates on the (112) surface of tungsten and molybdenum, which were carried out earlier [6, 7, 9, 11]. The common characteristic features of SD of adatoms in the systems Li–W(112), Li–Mo(112), Sr–W(112), Sr–Mo(112), and Dy–Mo(112) are, first, that the diffusion coefficients are minimal

in the PT-I regions, and, secondly, that the diffusion coefficients increase rapidly as the coverage grows in the range $\theta > 0.45$, i.e. in the C-I-transition region. The latter effect, which we connect with the transition to the soliton mechanism of diffusion discussed above, is more pronounced for molybdenum than for tungsten. The basic differences between Li and Sr diffusion on both substrates might be caused by the difference between the radii of those adatoms, as well as by peculiarities of the interaction between adatoms themselves and that between adatoms and substrate atoms. Sr atoms, due to their large dimensions ($r_{\text{Sr}} = 2.15 \text{ \AA}$), start building up the second physical monolayer already at $\theta_{\text{Sr}} > 0.72$, while the second physical monolayer of lithium ($r_{\text{Li}} = 1.51 \text{ \AA}$) starts its formation only after the coverage $\theta_{\text{Li}} \approx 1.9$ having been formed (see section 2. and Fig. 1). At $\theta < 0.45$, the activation energy of SD of strontium on both substrates is by 0.3–0.4 eV (approximately by a factor of 1.5) higher than that of lithium. This testifies to that the higher sensibility of the adsorption energy for a strontium atom to its position on the substrate may be owing to the greater contribution of the directed (covalent) component to the coupling between the alkaline-earth adsorbate and the substrate. Therefore, as the coverage is approaching a dense (incommensurate) monolayer, the difference between the adsorption and diffusion activation energies for strontium, as well as for other alkaline- and rare-earth adsorbates, becomes small. Under such conditions, diffusion is accompanied by intense desorption, so that it is practically impossible to observe diffusion of those adsorbates over macroscopic distances in a reasonable time of experiment [9]. Contrary to this, lithium (an alkaline element) readily diffuses over macroscopic distances at any coverages.

4.3. Comparison of the diffusion parameter values determined in the absence and the presence of the electric field

Earlier, the surface diffusion of lithium on the (112) surface of tungsten was studied using the field emission fluctuation method on tungsten microcrystals (tips) in a field emission microscope [34]. It is accepted that only few point defects can exist on the microcrystal planes [19], whereas more defects may be present on macrocrystals, especially the linear ones, such as atomic steps and grain boundaries. It is evident that the number of defects depends on the methods of surface treatment and preparation of specimens for experiment. Modern technologies cannot ensure a perfect macrosurface.

Therefore, one should take into account that defects can influence the surface processes. This issue attracts a significant attention when studying the surface diffusion. As a rule, defects create additional potential barriers for diffusion [22, 35]. Therefore, one may expect that, owing to the influence of defects on macrocrystals, the activation energy would be higher, while the diffusion coefficient lower, than the corresponding values on more perfect surfaces of microcrystals. However, a comparison of our results with the data concerning diffusion on microcrystals [34] evidences against this assumption: provided identical concentrations and temperatures, the diffusion coefficients of lithium on a tungsten macrocrystal are approximately three orders of magnitude as large as those on microcrystals (Fig. 5). Moreover, the temperature range of diffusion on the macrocrystal investigated by us was considerably wider than that in work [34]. According to what was told above, defects can hardly be responsible for such discrepancies.

In our opinion, a more probable reason for the strong difference between the diffusion coefficients determined by the compared methods might be, first of all, the distinction of conditions under which the SD process was studied. In the SCPM method applied by us, the evolution of concentration profiles is registered under conditions, where *the electric field is practically absent near the surface*. In the framework of the fluctuation method, on the contrary, recorded are the fluctuations of the field-emission current, from which the data on the kinetics of formation and relaxation (through diffusion) of the adatom concentration fluctuations in the equilibrium film are extracted afterwards. Therefore, these data *characterize the kinetics of diffusion in the electric field with a strength of about $3 \times 10^7 \text{ V/cm}$ oriented towards the surface*.

Let us consider the influence of the field on the activation energy of diffusion in more detail. A considerable reduction of the surface work function that accompanies the adsorption of electropositive metals, including lithium, testifies to that adatoms (to be more exact – the adsorption bond) have in this case a significant dipole moment. Its positive pole is oriented away from the surface (Fig. 11). The variation of the adatom potential energy under the action of the electric field can be described by the expression

$$\Delta E_a = E_a^F - E_a^0 = -(\mathbf{p}\mathbf{F}) - \alpha F^2/2, \quad (1)$$

where E_a^0 and E_a^F are the adsorption energies in the absence and in the presence of the field, respectively; \mathbf{p} is the dipole moment; α is the adatom polarizability;

and \mathbf{F} is the strength of the electric field [36, 37]. We note that the energy is reckoned from the vacuum level ($E = 0$); therefore, its value for the adsorbed state is negative. The polarizability of alkaline atoms, including lithium, in the adsorbed state was shown to be low [38]. Therefore, the quadratic-in-the-field term in formula (1) can be neglected, so that

$$\Delta E_a \approx -(\mathbf{p}\mathbf{F}). \quad (2)$$

The dipole moment of an electropositive adatom and the electric field that causes the electron field emission (the tip being charged negatively at that) are the antiparallel vectors (Fig. 11). Therefore, the value of ΔE_a is positive in this case, and the curve that reflects the potential relief of the surface for an adatom is shifted upwards on the whole. However, the local strength of the electric field is higher when the adatom is situated at the saddle point rather than in the “well”. Accordingly, the energy variation under the action of the field has to be larger in the first case (it should be even greater if one takes into account that the value of the dipole moment at the saddle point has to exceed its value in the well). As a result, the activation energy of diffusion E_d , i.e. the difference between the adatom energies in the well and at the saddle point, should grow. Indeed, in work [39], the activation energy of the potassium diffusion on tungsten was found to increase in the field, at which the field emission took place. Thus, the effect discussed can explain why the diffusion of lithium observed in our “zero-field” experiments occurs at the temperatures lower than those in experiments carried out with a field emission microscope. It is evident that the influence of the field on the kinetics of diffusion is a subject of interest by itself.

5. Conclusions

1. Within the range of the first monolayer, the diffusion coefficient of lithium on the (112) surface of tungsten changes by more than an order of magnitude. This is a manifestation of both the lateral interaction of adatoms and the collective character of surface diffusion mechanisms. At the small and medium coverages, the collective mechanisms are realized through the diffusion of clusters, as well as the processes of two-dimensional evaporation and condensation in the region of the first-order phase transition. While the coverage is approaching a dense monolayer and the adatoms start to form structures incommensurate with the substrate,

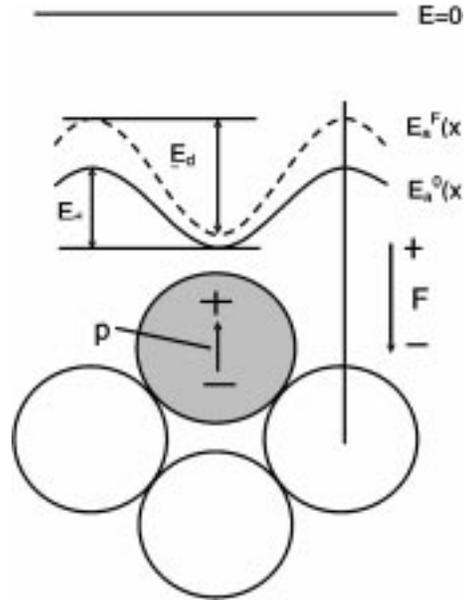


Fig. 11. Energy diagram of the variation of the adsorption energy of an adatom with the dipole moment \mathbf{p} under the action of the electric field \mathbf{F}

the topological solitons are formed in the adlayer and the diffusion coefficient steeply increases due to high soliton mobility. These regularities of diffusion are common for all alkaline, alkaline-earth, and rare-earth adatoms investigated in our works.

2. Owing to the large difference of the diffusion parameters characteristic of various film phases, there occurs a dynamic self-organization of the diffusion zone — the formation of separate areas in it which correspond to various phase states of the film. This process is affected substantially by the initial conditions, the temperature, and the time of diffusion. The phase structuring of the diffusion zone is more pronounced at low temperatures and longer diffusion times. Actually, this process can be considered as a manifestation of the two-dimensional reaction diffusion, bearing in mind that the result of the reaction between the adsorbate and the substrate is the formation of one or another two-dimensional phase with definite stoichiometry and structure. Not only does the rate of mass transfer govern the zone evolution kinetics but also the kinetics of both the nucleation of new phases and the processes running at their interfaces. It should be taken into account as well that the structure of a substrate itself can change in the course of diffusion, owing to the chemical interaction of the substrate with an adsorbate and due to the action of stresses caused by the presence of the adsorbed film and concentration gradients in it.

3. The comparison of the diffusion parameters obtained by the method of contact potential difference and the method of fluctuations of the electron field emission current allows us to conclude that the method of fluctuations gives the underestimated values of the diffusion coefficient owing to the influence of the high electric field near the surface, which is characteristic of this method.

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ПОВЕРХНЕВА ДИФУЗІЯ В СУБМОНОШАРОВИХ ПЛІВКАХ ЛІТІЮ НА ГРАНІ (112) ВОЛЬФРАМУ

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Резюме

За допомогою методу контактної різниці потенціалів досліджено кінетику поверхневої дифузії в субмоношарових плівках літію на грані (112) вольфраму. Одержані експериментальні дані свідчать про колективний характер поверхневої дифузії, який спричиняє сильні зміни дифузійної кінетики при зміні концентрації адсорбованих атомів на поверхні і динамічну самоорганізацію дифузійної зони. Порівнюються концентраційні залежності параметрів дифузії різних електропозитивних адсорбатів і обговорюються їх загальні риси та відмінності. Обговорюється також вплив електричного поля на кінетику поверхневої дифузії.

ПОВЕРХНОСТНАЯ ДИФФУЗИЯ В СУБМОНОСЛОЙНЫХ ПЛЕНКАХ ЛИТИЯ НА ГРАНИ (112) ВОЛЬФРАМА

А.Т. Лобурець, Н.Б. Сененко, Ю.С. Ведула, А.Г. Наумовець

Резюме

С помощью метода контактной разности потенциалов исследована кинетика поверхностной диффузии в субмонослойных пленках лития на грани (112) вольфрама. Полученные экспериментальные данные свидетельствуют о коллективном характере поверхностной диффузии, который обуславливает сильные изменения диффузионной кинетики при изменении концентрации адсорбированных атомов на поверхности и динамическую самоорганизацию диффузионной зоны. Сравняются концентрационные зависимости параметров диффузии различных электроположительных адсорбатов и обсуждаются их общие черты и отличия. Обсуждается также влияние электрического поля на кинетику поверхностной диффузии.