INFLUENCE OF COADSORBED STRONTIUM ATOMS ON SURFACE DIFFUSION IN LITHIUM SUBMONOLAYER FILMS ON TUNGSTEN (112) FACE

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The surface diffusion of lithium atoms in coadsorbed Li–Sr submonolayers on the atomically anisotropic tungsten (112) face is studied, by using the method of scanning contact-potential microscopy. The influence of strongly bound and less mobile Sr adatoms on the diffusion kinetics of more mobile Li atoms is analyzed. Coadsorbed strontium atoms are found to strongly suppress the diffusion of lithium ones. The concentration dependences are obtained for the chemical diffusion coefficients, activation energy, and pre-exponential factor in the Arrhenius equation. Possible mechanisms of surface diffusion in coadsorbed films are considered, by taking the nature of the lateral interaction between adatoms into account, which is responsible for the formation of long-period chain structures. A conclusion is drawn that the collective mechanisms of diffusion, which give rise to the exponential growth of diffusion coefficients, become active as the lithium coverage degree increases so that the film becomes structurally incommensurate with the substrate. The results obtained can be applied to the development of technologies for the modification of physico-chemical properties of surfaces.

1. Introduction

Multicomponent adsorbed monolayers are specific objects, whose physical and chemical properties are governed by the interaction between every of the components and the substrate, as well as by the interaction of adsorbed particles (adparticles), which can be of either an identical or different chemical nature. In practice, the problem concerns most often just multicomponent adsorption systems. Quite often, the addition of even the insignificant amount of an impurity into a monolayer can strongly affect the catalytic activity, work function, diffusion kinetics, and other physico-chemical parameters of the surface. On the one hand, this circumstance allows the surface to be modified purposefully. On the other hand, a noncontrollable deposition of impurities onto the surface can lead to undesirable effects.

It should be noted that, in various practical problems, the opposite requirements concerning the direction of a surface modification are often put forward. For instance, to stimulate catalytic reactions or to create conditions for the self-assembling of a monolayer, it is necessary to provide a high enough mobility of adparticles. On the contrary, the high surface mobility can negatively affect the stability and the service life of nanodevices and nanomaterials.

It is evident that a comprehensive study of factors that govern the properties of multicomponent adlayers is rather a challenging problem. Till now, these factors have been studied much less than those in the case of one-component monolayers, which is associated with a much more complicated character of multicomponent monolayer structures and interactions in such monolayers.

This work is aimed at studying some characteristics of the surface diffusion in a model two-component system, namely, lithium and strontium films coadsorbed on the (112) face of a tungsten crystal. Both adsorbates are electropositive metals – lithium is an alkaline element, and strontium is an alkaline-earth one – but their atomic radii strongly differ from each other: $r_{\mathrm{Li}} = 1.55$ Å and $r_{\mathrm{Sr}} = 2.15$ Å. The W(112) face has a strongly anisotropic structure, which is formed by alternating densely packed rows of tungsten atoms and grooves of atomic depth (see Fig. 1). This substrate was used in our previous works to study the kinetics of surface diffusion of lithium and strontium atoms separately in detail [1, 2]. We found that, at the same temperature, the mobility of Li atoms was several orders of magnitude higher than that of Sr ones. A number of preliminary data were also obtained, which testified that the presence of coadsorbed Sr atoms on the surface inhibits the mobility of Li adatoms [3]. In this work, we report the results of a more detailed research of this effect. The concentration dependences of the diffusion coefficients of lithium are obtained for

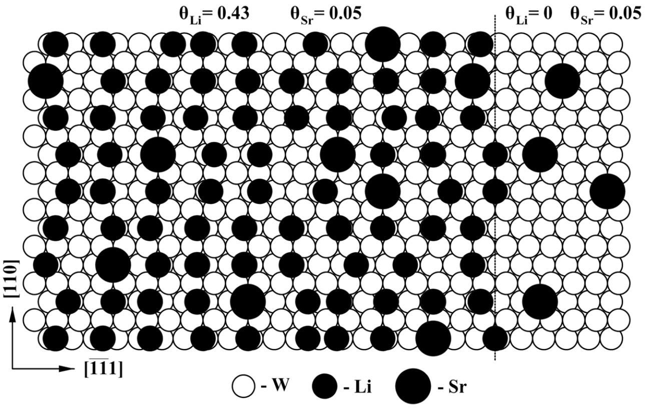

Fig. 1. Diagram of the tungsten (112) face structure. Hollow circles denote tungsten atoms; small and large solid circles denote adsorbed lithium and strontium atoms. $\theta_{\mathrm{Li}} \approx 0.43$ and $\theta_{\mathrm{Sr}} \approx 0.05$. The edge of the lithium concentration stair is marked by a dotted line. The film in the figure is assumed to be structurally noncoherent with the substrate. The long-range order is absent, but the orientational order does take place

three different strontium coverages. The dependences of the activation energies and the pre-exponential factors in the Arrhenius equation, which describes the temperature dependence of the lithium diffusion coefficient, on the coverage degree are determined.

2. Research Methods

To study the surface diffusion, the method of scanning contact-potential microscopy is applied. It is a nondestructive technique, which allows the evolution of specially formed concentration profiles of an adsorbate to be studied at various temperatures. The local concentration is determined by scanning the surface with a narrow beam of low-energy electrons and measuring the local work function, which depends on the concentration. The spatial resolution of the method is about 1 μm, and the determination accuracy for the degree of surface coverages with lithium and strontium ranged within the limits from 0.01 to 0.05 monolayer. The coverage degree of the surface with an adsorbate was defined as the ratio between the corresponding adatom concentration and the surface concentration of tungsten atoms, i.e. $\theta_{\mathrm{Li}} = n_{\mathrm{Li}}/n_{\mathrm{W}}$ for lithium atoms and $\theta_{\mathrm{Sr}} = n_{\mathrm{Sr}}/n_{\mathrm{W}}$ for strontium ones. At such a definition, the coverage, for which $\theta = 1$, is called a geometric monolayer. For the tungsten (112) face, $n_{\mathrm{W}} = 8.2 \times 10^{14}$ cm^{-2}. We emphasize that, in this work, all experiments were carried out using submonolayer coverages, i.e. $\theta < 1$.

The setup of our experimental installation was described in work [4]. Measurements were carried out under ultrahigh vacuum of $10^{-11} - 10^{-12}$ Torr. A single-crystalline tungsten wafer 0.07 mm in thickness and 8×3.2 mm^2 in size served as a substrate. The accuracy of the surface plane orientation with respect to the [112] direction was $\pm 20'$. The description of other experimental details such as Li and Sr evaporators, procedures of tungsten crystal degassing and carbon removal, calibration techniques for Li and Sr atomic beams, work function measurements, and creation of adsorbate concentration profiles on the substrate surface can be found in our previous works [1, 2, 5, 7].

The increase in the coverage degree, when Li and Sr atoms are adsorbed onto W crystal faces, is known to be accompanied by a reduction in the surface work function by several electronvolts owing to a strong polarity of the adsorption bond. This circumstance enables one, by measuring – in a series of experiments for pure or mixed films with known compositions – the dependence of the work function on the coverage degree, to recalculate the two-dimensional distributions of local work-function values, $\phi(x, y)$, into the corresponding distributions of the coverage degree, $\theta(x, y)$.

If the temperature is not too high, the mobility of lithium adatoms is much higher than that of strontium ones [1, 2]. This results in a strong difference between the surface diffusion parameters for lithium and strontium adatoms on the W(112) face. Taking advantage of this fact, it is easy to choose a temperature interval, in which the diffusion of strontium in a binary submonolayer Li–Sr film can be neglected. Actually, under such conditions, strontium atoms play the role of point defects-stoppers for the diffusion of lithium. The concentration of such defects can be easily controlled by varying the Sr sputtering dose. It is essential to emphasize that the atomic relief of the W(112) face is substantially anisotropic (see Fig. 1), and, as a result, adatoms diffuse much faster along densely packed atomic grooves. Our experiments were carried out in such a geometry that just the process of lithium diffusion along the grooves was observed (see below). Under such conditions, lithium atoms were forced to move purposefully toward defects, which were also located in the grooves, so that the influence of defects could manifest itself especially strongly (Fig. 1).

When being adsorbed on the tungsten (112) face, lithium and strontium atoms form long-period structures of the same type $p(1 \times N)$, where N is an integer number, oriented along the [110] direction, i.e. normally to

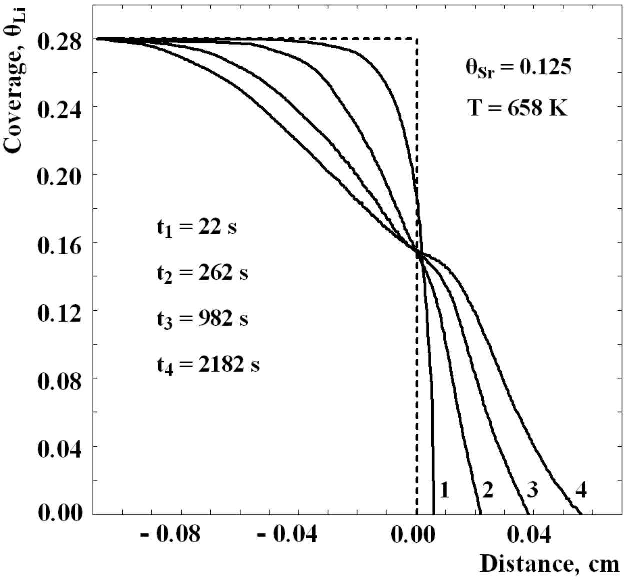

Fig. 2. Lithium concentration profiles in the course of the diffusion evolution against the background of a strontium pedestal at $\theta_{\rm Sr}^{\rm fix} = 0.125$. The stair edge (the dotted line) corresponds to the Matano line

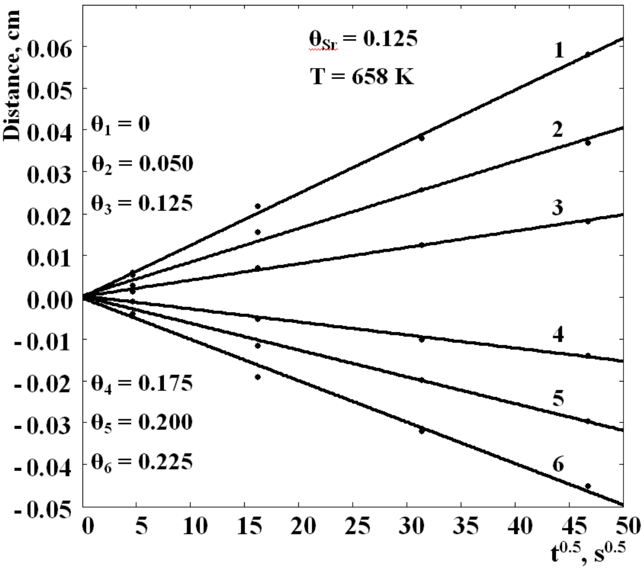

Fig. 3. Dependences of the front displacement for the lithium concentration distribution in a coadsorbed Li–Sr–W(112) film on $t^{0.5}$ at various coverages. Lines are plotted using the results presented in Fig. 2

the atomic grooves on the substrate (Fig. 1). The thermal stability of those structures is higher for strontium [8, 9]. Note that we studied the diffusion at temperatures, when the long-range order in adsorbed Li and Sr films did not exist anymore, but the short-range one still could take place.

To carry out the diffusion experiments in binary Li–Sr films, the whole surface of the crystal was firstly covered uniformly with a background strontium film to a certain fixed coverage $\theta_{\rm Sr}^{\rm fix}$; in such a way, the strontium concentration "pedestal" was formed. Afterward, half a crystal surface prepared in that way was sputtered with a lithium film, which had a sharp boundary oriented perpendicularly to the [111] direction, i.e. to the groove direction. As a result, the lithium concentration "stair" was created (Fig. 1). The distributions of local work function values $\phi(x, y)$ obtained owing to the lithium diffusion from stair-like initial coverages at various temperatures and fixed strontium coverages were recalculated into concentration profiles. For the determination of the concentration dependences of the diffusion coefficients, we used the Boltzmann–Matano method [10]. In such a manner, we experimentally determined the so-called chemical diffusion coefficients of lithium on the W(112) surface previously covered with a certain given amount of strontium (to a submonolayer coverage degree).

Temperature intervals, in which diffusion experiments were carried out, were limited by two factors. The restriction from above (at high temperatures) arose owing to the necessity to use short time intervals at the diffusion annealing; those intervals were of about several seconds and close to the time of the warming up of a specimen. At low temperatures, the time of the diffusion annealing grew up to several hours. Therefore, there emerged a danger that the adsorbed film would be contaminated by residual gases.

3. Experimental Results and Their Discussion

3.1. Shape and time evolution of concentration diffusion profiles

In Fig. 2, the examples of lithium concentration distributions in the diffusion zone at the background strontium concentration $\theta_{\rm Sr}^{\rm fix} \approx 0.125$ are depicted. Their shapes obviously differ from the classical shape typical of the diffusion distribution for noninteracting particles. This fact testifies to a strong concentration dependence of lithium diffusion coefficients. Here, it is of importance to elucidate, whether the diffusion zone will expand following the law $t^{0.5}$, because the application of the Boltzmann–Matano method for the determination of diffusion coefficients is eligible only provided that this condition is satisfied. Otherwise, the diffusion coefficients will be dependent on the time or/and coordinate, i.e. the diffusion may turn out abnormal.

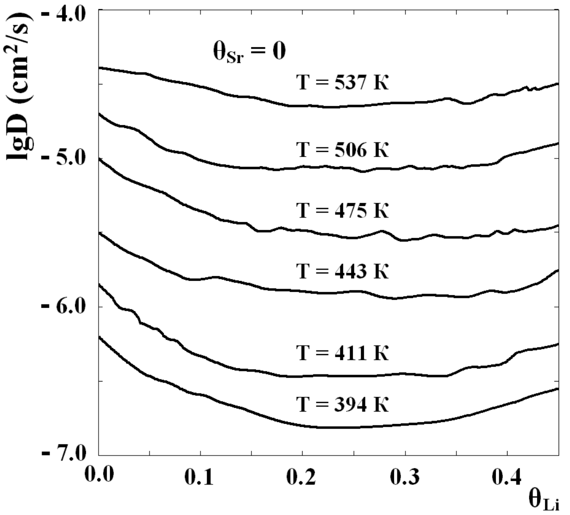

Fig. 4. Dependences of the lithium diffusion coefficients on the coverage degree $\theta_{\rm Li}$ in the Li–W(112) system at various temperatures T

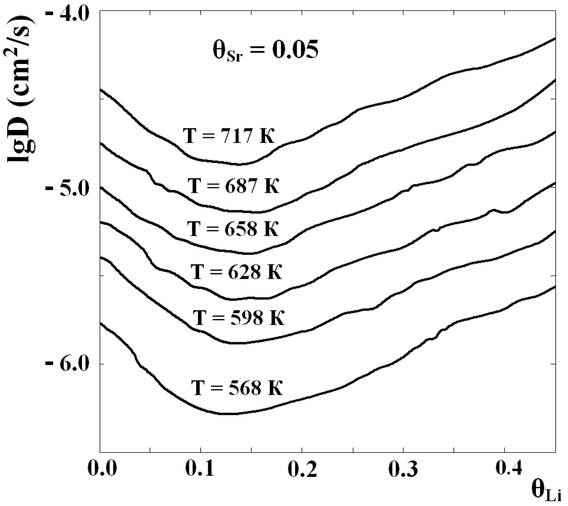

Fig. 5. Dependences of the lithium diffusion coefficients on the coverage degree $\theta_{\rm Li}$ in the Li–Sr–W(112) system with $\theta_{\rm Sr}^{\rm fix} = 0.05$ at various temperatures T

As follows from Fig. 3, the evolution of the lithium diffusion distributions occurs practically in the framework of the "normal" scenario, i.e., to a satisfactory accuracy, the profiles are invariant in the coordinates $(x/t^{0.5}, \theta)$. This fact enabled us to use the Boltzmann–Matano method for the calculations of the concentration dependences of the diffusion coefficient by analyzing the shape of diffusion profiles. This method includes the calculation of the derivative $d\theta/dx$ from the experimentally obtained local values of work function recalculated into the coverage degrees. There is a certain θ-spread (noise), which can be determined from the experiment. This phenomenon is associated with defects of the substrate surface and with fluctuations of the work function itself. Therefore, the differentiation procedure cannot be carried out without a preliminary smoothing of the $\theta(x)$-distributions. After substituting the experimentally obtained θ-profiles by analytical functions (splines), the differentiation and integration steps can be chosen arbitrarily.

3.2. Influence of coadsorbed strontium on the lithium diffusion coefficients

Figures 4 and 5 demonstrate the concentration dependences of the diffusion coefficient D of lithium on a pure W(112) surface and on the same surface previously covered with strontium to $\theta_{\rm Sr}^{\rm fix} = 0.05$ obtained at various temperatures T. A comparison of those results testifies that even a small amount of strontium atoms in the adsorption system Li–Sr–W(112) not only strongly reduces the lithium diffusion coefficients (by approximately two orders of magnitude at identical temperatures), but also leads to appreciable qualitative changes in the concentration dependences of D. At high temperatures and the coverages $\theta_{\rm Li} < 0.5$ in pure lithium films, the diffusion coefficients depend rather weakly on the concentration (Fig. 4). As the temperature decreases, this dependence becomes stronger, the wide minimum gets narrowed and becomes localized in the range $0.2 < \theta_{\rm Li} < 0.3$. Another scenario is observed in a coadsorbed film. Figure 5 exhibits the dependences $\lg D(\theta_{\rm Li}, \theta_{\rm Sr}^{\rm fix})$ obtained at the fixed coverage value $\theta_{\rm Sr}^{\rm fix} \approx 0.05$ and various temperatures. Every of them reveals a well-pronounced minimum in the interval $0.12 < \theta_{\rm Li} < 0.15$ followed by a strong (exponential) growth of the diffusion coefficients: the growth of $\theta_{\rm Li}$ is accompanied by an almost linear increase of $\lg D$. A similar character of growth is observed for a pure lithium film as well; however, this effect is observed at much higher coverages, $\theta_{\rm Li} > 0.5$ [2].

All those differences for the lithium diffusion in pure and coadsorbed films can take place not only owing to the lateral interaction, but also to the phase state of the film and the mechanisms of surface diffusion. The weak concentration dependence of the diffusion coefficients in pure lithium films at $\theta_{\rm Li} < 0.5$ may be associated with the fact that the temperature interval selected for diffusion researches was located well above the critical temperature, and the film was homogeneous under such conditions, being a two-dimensional gas, the properties of which approaches those of the ideal gas, as the temperature grows. However, if the temperature decreases and

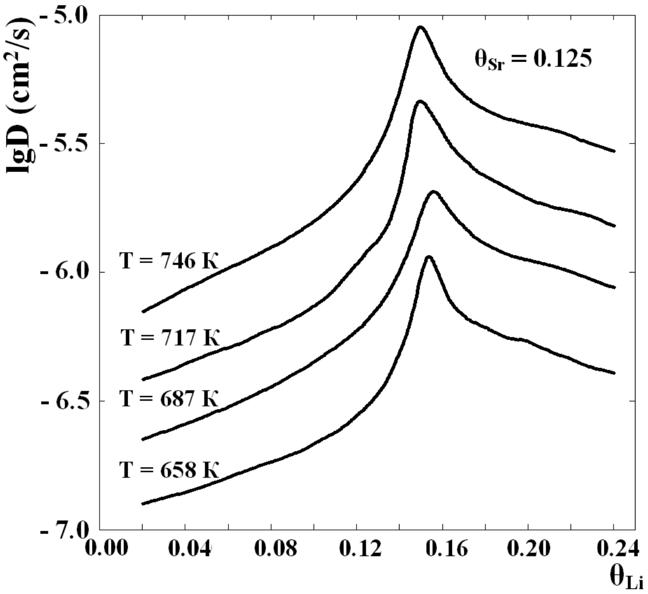

Fig. 6. Dependences of the lithium diffusion coefficients on the coverage degree $\theta_{\rm Li}$ obtained at $\theta_{\rm Sr}^{\rm fix} = 0.125$

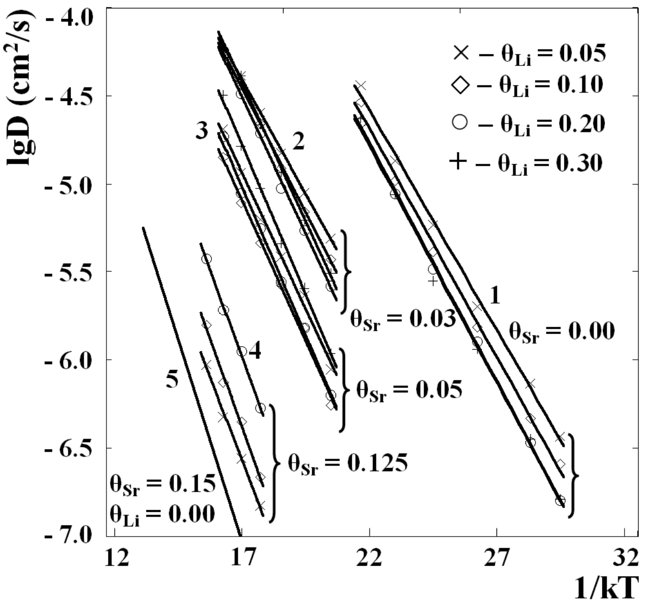

Fig. 7. Arrhenius plots for diffusion coefficients in various adsorption systems: Li–W(112) (*1*); Li–Sr–W(112), $\theta_{\rm Sr} = 0.03$ (*2*); Li–Sr–W(112), $\theta_{\rm Sr} = 0.05$ (*3*); Li–Sr–W(112), $\theta_{\rm Sr} = 0.125$ (*4*); and Sr–W(112), $\theta_{\rm Sr} = 0.15$ (*5*)

the coverage degree increases, the role of the lateral interaction between lithium adatoms grows, as it must be in the case of a real gas, which affects the character of $\lg D(\theta_{\rm Li})$-dependences (Fig. 4).

Lithium and strontium diffusion in pure films on the atomically anisotropic (112) faces of tungsten and molybdenum at low enough temperatures occurs owing to the motion of adatoms along atomic grooves on the substrate, i.e. the motion is quasi-one-dimensional [11, 12]. This circumstance is related to high potential barriers for the movement of adatoms across the grooves. At the coadsorption, strontium adatoms, which are strongly bound to the substrate (the adsorption energy is about 3.6 eV), block the grooves and, in such a manner, the lithium diffusion as well (Fig. 1). Therefore, in order to obtain the concentration profiles with macroscopic dimensions, the temperature has to be elevated. It is evident that, under such conditions and at low $\theta_{\rm Li}$-coverages, lithium atoms can individually bypass strontium ones, by climbing onto the groove "crest" or even by moving to the neighbor groove, which naturally requires a higher activation energy. At $\theta_{\rm Sr}^{\rm fix} \approx 0.125$, the character of concentration dependences of diffusion coefficients changes drastically. In Fig. 6, the corresponding dependences obtained at various temperatures are shown. As was already noted, at a small amount of strontium ($\theta_{\rm Sr}^{\rm fix} \leq 0.05$), the minimum in the dependence $\lg D(\theta_{\rm Li})$ gets narrowed and shifted toward low lithium coverages, whereas its depth grows. However, at $\theta_{\rm Sr}^{\rm fix} \approx 0.125$, the D-minimum disappears altogether. Under those conditions, the plots $\lg D(\theta_{\rm Li}, \theta_{\rm Sr}^{\rm fix})$ contain a section at $\theta_{\rm Li} < 0.1$, where $\lg D$ grows almost linearly; then, the growth becomes superlinear; and, at $\theta_{\rm Li} = 0.155$, there emerges a new peculiarity, which looks like a strongly pronounced maximum. A possible origin of such modifications will be discussed in section 3.4.

3.3. Activation energies and pre-exponential factors in the Arrhenius equation for the lithium diffusion

The Arrhenius plots $\lg D = f(1/T)$ for a pure adsorption systems Li–W(112) and in the presence of strontium in concentrations that correspond to $\theta_{\rm Sr}^{\rm fix} = 0.03$, 0.05, and 0.125 are shown in Fig. 7. The lines are grouped in accordance with the lithium coverages $\theta_{Li} = 0.05$, 0.1, 0.2, and 0.3. Line 5 corresponds to the temperature dependence of the strontium diffusion coefficient in the pure system Sr–W(112) at $\theta_{\rm Sr} \approx 0.15$. The experimental points were fitted quite satisfactorily by straight lines, which allowed us to determine the diffusion activation energy E_d and the pre-exponential factors D_0.

The concentration dependences of the activation energy for five adsorption systems are depicted in Fig. 8. Curves 1 and 5 correspond to pure lithium and strontium, respectively, films on the tungsten (112) face.

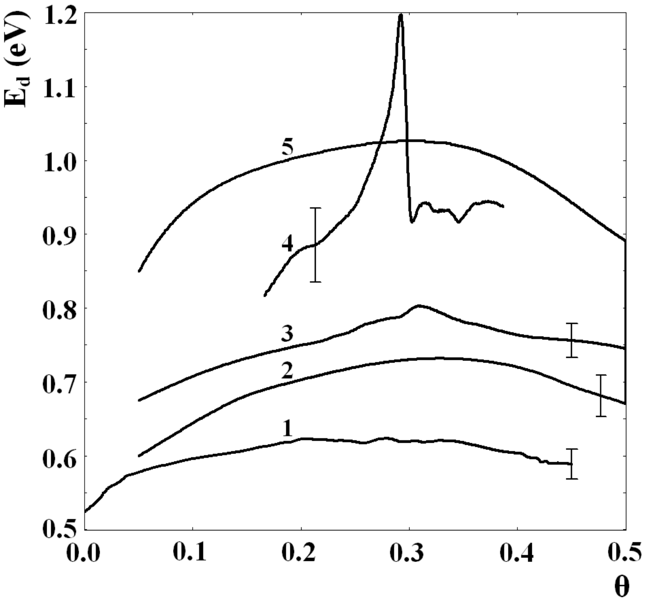

Fig. 8. Dependences of the activation energy on the total coverage degree $\theta = \theta_{\rm Li} + \theta_{\rm Sr}$ for five various adsorption systems: Li–W(112) (*1*); Li–Sr–W(112), $\theta_{\rm Sr} = 0.03$ (*2*); Li–Sr–W(112), $\theta_{\rm Sr} = 0.05$ (*3*); Li–Sr–W(112), $\theta_{\rm Sr} = 0.125$ (*4*); and Sr–W(112) (*5*)

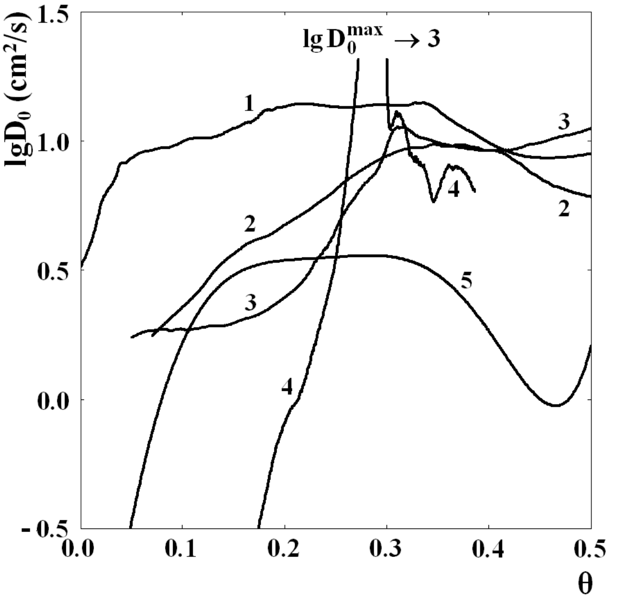

Fig. 9. Dependences of the pre-exponential factor in the Arrhenius equation on the total coverage degree θ. The notations of curves are the same as those in Fig. 8

Curves *2, 3*, and *4* describe binary films with the strontium contents corresponding to coverages of 0.03, 0.05, and 0.125, respectively. As one can see, the strontium content in the adsorbed film increases with the activation energy. The maximum values of activation energy are observed at coverages within the interval $\theta \approx 0.25 \div 0.35$ for all plots, where $\theta = \theta_{\rm Li} + \theta_{\rm Sr}$ is the total coverage degree. The average magnitudes of the determination error for E_d are marked in the plot by "whiskers". An interesting feature is observed in curve *4* at $\theta_{\rm Li} \approx 0.155$ ($\theta \approx 0.28$). Here, the maximum of E_d is expressed well enough, and it correlates with maxima in the concentration dependences of the lithium diffusion coefficients at $\theta_{\rm Sr}^{\rm fix} \approx 0.125$ (Fig. 6). As the temperature grows, the coverage values, at which the inflection points appear in diffusion profiles, drift a little toward low lithium concentrations. In addition, the positions of diffusion coefficient maxima are affected by errors admitted at the strontium sputtering to $\theta_{\rm Sr}^{\rm fix} \approx 0.125$ in different experiments. Therefore, the accuracy of the determination of the activation energy in the range, where the maximum of $E_d(\theta)$ exists, was approximately ±0.15 eV, which is much worse than the error obtained in other sections (±0.05 eV).

In Fig. 9, the concentration dependences of the pre-exponential factors D_0 are shown. Curves *1* and *5* correspond to pure systems Li–W(112) and Sr–W(112), respectively. They are qualitatively similar to each other. Curves *2* to *4* correspond to coadsorbed systems with $\theta_{\rm Sr}^{\rm fix} = 0.03$, 0.05, and 0.125, respectively. One can see that, if Li and Sr are mixed, the dependences $\lg D_0(\theta_{\rm Li}, \theta_{\rm Sr}^{\rm fix})$ change drastically; in particular, D_0 diminishes considerably at low lithium coverages. This fact can be associated with a change of the entropic factor, as the parameter $\theta_{\rm Sr}$ grows, because strontium adatoms reduce the number of degrees of freedom for lithium ones, and, as a result, the variation of the activation entropy ΔS becomes negative. Moreover, the presence of stoppers on the surface brings about a reduction in the probability for lithium atoms to make long jumps [14].

Curves *2* to *4* in Figs. 8 and 9 reveal maxima of E_d and D_0, respectively, in the interval of total coverage $0.25 < \theta < 0.35$. In the cases $\theta_{\rm Sr}^{\rm fix} = 0.03$ and 0.05, (curves *2* and *3*, respectively), the maxima are observed rather badly, but they become very sharp at $\theta_{\rm Sr}^{\rm fix} \approx 0.125$ (curves *4*). In Fig. 9, this maximum was even truncated, but we marked there that the corresponding value of $\lg D_0^{\rm max}$ tends to three. In general, if comparing with a pure lithium film, the section, where the lithium diffusion coefficient increases exponentially in mixed Li–Sr films shifts toward low coverages, when the strontium content increases (see Figs. 4 to 6). This effect is most probably related to changes in the character of the interaction between adatoms and in the film structure, which can induce a change of the diffusion mechanism. Let us consider this issue on the basis of results obtained in our previous works.

3.4. Relation between diffusion parameters and the structure of adsorbed Li and Sr films

Let us recall some information concerning the structure of two-dimensional lithium and strontium films on the tungsten (112) face, which was obtained in works [8, 9] with the use of the low-energy electron diffraction technique. The formation of long-period chain superstructures $p(1 \times 4)$ and $p(1 \times 7)$ in lithium and strontium films adsorbed onto the W(112) face testifies that the interaction forces between those adatoms in the [111] direction, i.e. along the grooves, fall down slowly and nonmonotonically [15]. Such structures are commensurate with the substrate, because their periods are multiples of the periods of the substrate surface lattice. If the concentration of adatoms grows, their interaction becomes stronger, and they minimize the free energy by forming the new denser phases by means of a phase transition of the first order. Just this process takes place in lithium and strontium films at $\theta < 0.5$ [8, 9]. A further film densification, when the parameter θ increases, takes place owing to the phase transition of the second order, which means the violation of the structural commensurability between the films and the substrate (the commensurate–incommensurate (C–I) transition). At its initial stage, the commensurability is destroyed locally in domain walls (misfit dislocations) that separate commensurate domains. These walls have the properties of topological solitons, are characterized by a high mobility, and serve as effective mass carriers in the course of diffusion through the commensurate phase [16]. In pure lithium and strontium films on the W(112) face, the C–I transition occurs at $\theta > 0.5$ [8, 9], and, as a result of the strong atomic relief anisotropy of the substrate, the commensurability is violated only along the grooves, i.e. in the $[\bar{1}\bar{1}1]$ direction.

The ability of lithium and strontium to form long-period chain structures of the same type on the tungsten and molybdenum (112) faces at low temperatures brings about an idea that the corresponding coadsorbed films preserve this property. Although the film structures have not been studied hitherto in direct experiments, the assumption can be made with a high reliability that, on surfaces with a highly anisotropic structure, the face symmetry and the anisotropy of a lateral interaction should affect the character of thermal fluctuations and the arrangement of adatoms even at rather high temperatures, when the long-range order is already broken. However, the orientational order, at which adatoms are located in the substrate grooves and there exist chain fragments of various lengths (linear clusters) oriented perpendicularly to the grooves, will evidently be preserved (Fig. 1). The degree of their coordination with the substrate diminishes, as the coverage degree increases.

If being coadsorbed with lithium atoms, strontium ones can serve as the nucleation centers for binary linear clusters consisting of both lithium and strontium atoms. Such clusters will be dynamic at high temperatures. They undergo deformation, decay, and new formation; they walk randomly and diffuse under the action of the chemical potential gradient. When the total coverage degree and the relative concentration of components in the film change, the character of a lateral interaction also changes. When the temperature decreases, the clusters can grow up in the form of chains with different lengths oriented normally to the substrate grooves (Fig. 1). More massive strontium atoms ($m_{\mathrm{Sr}}/m_{\mathrm{Li}} \approx 13$), which have a considerable covalent component in the chemical bond, will hamper the cluster diffusion. Our assumption concerning the formation of “hybride” Li–Sr chains is based on the results of generalizations made in work [16]. Chains of alkaline-earth atoms are much more stable than those of alkaline ones. The destruction of chains is prevented due to the Coulomb repulsion between strongly polarized adatoms. Ultimately, if the concentration of preliminarily adsorbed strontium increases, the diffusion coefficient of lithium becomes practically equal to that of pure strontium [6]. In other words, under those conditions, strontium almost completely “imposes” its mobility on the whole binary film. This fact is illustrated in Figs. 4 to 7. (The more detailed data concerning the Sr diffusion on the W(112) surface can be found in work [2].)

Now, let us discuss the probable origins of the appearance of the sharp D_{Li} maximum at $\theta_{\mathrm{Li}} = 0.155$ and $\theta_{\mathrm{Sr}} = 0.125$ (Fig. 6). Similar peaks were observed in a number of one-component adfilms in the range of the C–I transition [5, 6]. Their appearance was explained on the basis of the soliton theory of diffusion [16]. Both the thermodynamic (a sharp jump of the chemical potential) and kinetic (the change of the diffusion mechanism) factors can contribute to the drastic increase of D [16, 17]. For instance, the transition from the “single-atom” to collective mechanism of diffusion can take place, at which the mobility of mass carriers strongly grows. As was already marked above, the solitons (incommensurate domain walls) can play the role of such carriers. Under such conditions, the diffusion activation energy is determined by the Peierls relief [16]. However, on a real surface, the solitons can be pinned at both intrinsic substrate defects and coadsorbed atoms strongly bound with the substrate (in our case, these are strontium adatoms). For a soliton to be stripped from a defect, the definite activation energy is needed. In this case, the pre-exponential factor should decrease as the concentration of defects grows, which is really observed at $\theta < 0.25$ (Fig. 9). However, if the total coverage $\theta > 0.3$, the D_0-values remain to be rather close to those, which correspond to pure lithium, at all considered $\theta_{\mathrm{Sr}}^{\mathrm{fix}}$. At the same time, the situation differs radically in the interval $0.25 < \theta < 0.3$ at $\theta_{\mathrm{Sr}}^{\mathrm{fix}} = 0.125$. It manifests itself in a swift growth of the diffusion coefficients and the pre-exponential factor in rather a narrow interval of concentrations against the background of a significant increase in the activation energy. From Fig. 6, it follows that, at $\theta_{\mathrm{Li}} = 0.155$, the diffusion coefficient of lithium is approximately 12 times higher than that at $\theta_{\mathrm{Li}} \rightarrow 0$. This maximum is attained, when the total coverage degree is $\theta = 0.28$. We may suppose that, under such conditions, the C–I transition starts in the binary film as well, or the commensurate (soliton) configurations are formed at high temperatures. It is evident that the strontium atoms also participate in the process of diffusive movements in such a film. Really, after lithium has been quickly desorbed, a certain redistribution of strontium occurs in the considered coverage range in the diffusion zone. This fact points to the participation of strontium in the process of chemical potential equilibration on the surface. It is worth to note that the diffusion acceleration is observed, when the activation energy increases (Fig. 8). This is possible only if the pre-exponential factor strongly grows simultaneously (Fig. 9).

4. Conclusions

The results obtained in this work for the Li–Sr–W(112) system in a wide interval of submonolayer coverages, together with the results of our previous experiments for other similar systems, allow us to draw a general conclusion about a strong influence of low-mobility adsorbed particles on the diffusion kinetics of more mobile particles coadsorbed with them. This influence is associated with the interaction between coadsorbed particles, especially when the lateral forces have a long-range character, and the collective mechanisms of surface diffusion [6,18]. At low coverage degrees and the repulsive interaction, a diffusing particle has opportunity to bypass low-mobility stoppers, and, in the case of attractive interaction, to neutralize them, for instance, by filling defects of the trap type. When the coverage degree increases, and the mechanisms of surface diffusion acquire a strongly expressed collective character (e.g., at a phase transition that violates the structural commensurability between the film and the substrate), low-mobility impurities in the film can invoke the pinning of mass carriers, which extends over considerable film regions. In the examined effects, the important role is played by the atomic structure of the substrate. This role is especially crucial, when the surface structure is anisotropic, and there are atomic channels on it, which serve as ways for the “easy” diffusion. In this case, blocking the channels with low-mobility impurities gives rise to a strong slowing-down of diffusion processes.

The regularities observed in the influence of coadsorbed impurities on the surface diffusion in the film can be used for a purposeful modification of physico-chemical properties of the surfaces.

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ВПЛИВ СПІВАДСОРБОВАНИХ АТОМІВ СТРОНЦІЮ НА ПОВЕРХНЕВУ ДИФУЗІЮ У СУБМОНОШАРОВИХ ПЛІВКАХ ЛІТІЮ НА ГРАНІ (112) ВОЛЬФРАМУ

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Резюме

Методом сканувальної контактно-потенціальної мікроскопії досліджено поверхневу дифузію літію у субмоношарових співадсорбованих плівках Li–Sr на атомно-анізотропній грані (112) вольфраму. Мета роботи – дослідження впливу сильно зв'язаних і менш рухливих адатомів (Sr) на кінетику дифузії більш рухливих адатомів (Li). Встановлено, що адатоми стронцію сильно пригнічують дифузію літію. Одержано концентраційні залежності хімічних коефіцієнтів дифузії, енергії активації і передекспонентного множника у рівнянні Арреніуса. Розглянуто можливі механізми поверхневої дифузії у співадсорбованій плівці із урахуванням характеру латеральної взаємодії адатомів, яка спричиняє утворення довгоперіодних ланцюжкових структур. Зроблено висновок про те, що зі збільшенням концентрації літію, коли плівка стає структурно несумірною з підкладкою, починають діяти колективні механізми дифузії, які зумовлюють експонентне зростання коефіцієнта дифузії. Результати можуть бути використані при розробленні технологій модифікації фізико-хімічних властивостей поверхонь.