Surface Diffusion and Phase Transitions in Ultrathin Films with Quasi-One-Dimensional Long-Period Structures

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The kinetics of surface diffusion in a submonolayer film with the structure p(1 × 4) on the (112) bcc crystal surface in the region of a second order phase transition is investigated by molecular dynamics method. It is shown that collective effects play an important role in the surface diffusion within films where long-period chain structures are present. This is due to the strong anisotropy of the surface atomic structure and lateral interaction of adatoms. Adatom chains which form a superstructure p(1 × N) block the path of easy diffusion of individual atoms along the substrate grooves. With increasing temperature, the diffusion coefficients increase rapidly because of the emergence of new vacancies in the chains. Domains of a chain-like structure incommensurate with the substrate are formed in the adsorbed film when passing through the critical temperature. The activation energy for diffusion decreases sharply at temperatures above the critical one. The commensurate islands gradually disappear in the presence of the incommensurate structure as the temperature increases. This increases the number of defects in the incommensurate chain structure. Collective effects in the adsorbed film play an important role even at high enough temperatures owing to fluctuations and destruction of interacting segments of the adatom chains.

Keywords: Ultrathin Films, Superstructure, Surface Diffusion, Phase Transitions, Cooperative Effects.

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1. INTRODUCTION

Monolayers of atoms adsorbed on single crystal surfaces are specific objects. Their physical and chemical properties are governed by the interaction with substrate as well as by interaction between adsorbed particles (adparticles), which can be of either an identical or different chemical nature [1]. There is a close relation between surface physical and chemical properties and the aggregate state of adsorbed films. The structural phase transitions in thin films are source of important information about nature and quantitative characteristics of adatom-adatom and adatom-substrate interactions [2].

Contrary requirements for direction of surface modification are often posed in various practical problems. For example, a sufficiently high adparticle mobility is necessary to stimulate catalytic reactions or create conditions for self-assembly of monolayers. In contrast, high surface mobility can adversely affect stability and useful life of nanodevices and nanomaterials. The addition of even small quantities of impurities into a monolayer can greatly affect the catalytic activity, the work function, the kinetics of diffusion and other physical and chemical characteristics of the surface. On the one hand, this allows an intentional modification of the surface. On the other hand, an uncontrolled adsorption of impurities on the surface can lead to undesirable effects.

The purpose of this work is to investigate, by molecular dynamics simulation, the surface diffusion of electropositive adatoms which form stochiometric chain structures p(1 × N) with long periods on anisotropic single crystal faces at low coverage degrees and temperatures, as well as the processes of thermal disordering of such structures. We discuss the nature of the relationship between changes in the surface diffusion parameters and phase transitions in the adsorbed films.

2. RESEARCH METHODS

The (112) surfaces of tungsten and molybdenum have strongly anisotropic structure and almost identical lattice parameters. As a result, adatoms diffuse much faster along densely packed atomic grooves [3, 4]. Adsorbing on the faces, many alkaline, alkaline-earth and rare-earth elements form long-period chain superstructures p(1×N) (N is an integer) of the same type. Chains orientate along the [110] direction, i.e. perpendicular to the atom grooves of the substrate [5].

Previously, we studied the surface diffusion of lithium and strontium on single crystal (112) surfaces of tungsten and molybdenum by scanning contact-potential microscopy [3, 4, 6, 7]. The experiments were performed at rather high temperatures under which the long-range order in the films was absent. We could not determine very low diffusion coefficients at such temperatures when the films still possess a long-range order. In this study, we applied the method of molecular dynamics to elucidate the mechanism of adatom surface diffusion with such parameters of lateral interactions and coverage degrees when long-period quasi-one-dimensional chain structure p(1 × 4) are formed in the adsorbed film. Such structures can exist in a very wide temperature range. For example, the long-period structure p(1×5) of Ba adatoms on (112) Mo was recorded by LEED even at temperatures of about 700 K [5]. Evidently the emergence of such superstructures in

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adsorbed films is the result of lateral attraction of neighboring atoms within the chain (direction [110]) and repulsion between the chains (direction [111]). Thermal destruction of these structures occurs *via* a second order phase transition [5]. To formulate a mathematical model, we took into account information gleaned in our works [7, 8] about the nature of lateral interactions, the structure of the film and surface diffusion of lithium on the (112) tungsten surface. The interaction of adatoms through the substrate elastic field was not considered. We are interested in a qualitative picture of lithium superstructure disordering and dependence of surface diffusion kinetics on order parameter in the adsorbed film.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Fig. 1a shows a simulated equilibrium low-temperature distribution of adatoms on an anisotropic surface in submonolayer film at $\theta = 0.25$ and T = 130 K. The chain structures $p(1 \times 4)$ exist in real adsorption systems Li-W (112) and Li-Mo (112) [1, 5]. At temperatures below the critical one, adsorbed film is a two-dimensional crystal. Chain coordinates do not change with time in direction [111] even at temperatures close

to critical one. As temperature increases, vacancy number in chains increases, but long-range order is preserved and atoms between the chains can fluctatively form nuclei of the $p(1 \times 2)$ structure. Diffusion occurs by a kind of vacancy mechanism, in which the vacancies intrude into the chains and shift the adatoms to neighboring sites thereby forming kinks [9]. An average relative density of adatoms, forming a chain, can be taken as an order parameter in the adsorbed film. This parameter always fluctuates relative to some average value decreasing with increasing temperature.

Information about the thermal disordering of two-dimensional crystal can be obtained by recording the coordinates of each chain, taking into account the relative density of the location of adatoms in the chains as a function of discrete time. Such a result is illustrated in Fig. 2.

The domains incommensurate with the substrate structure begin to appear in the adsorbed film at temperatures higher than the critical one and stochiometric coverage $\theta_{Li} = 0.25$. The two-dimensional crystal becomes effectively free. With increasing temperature, the probability of occurrence and duration of the existence of domains with the structure $p(1 \times 4)$ are gradually reduced.
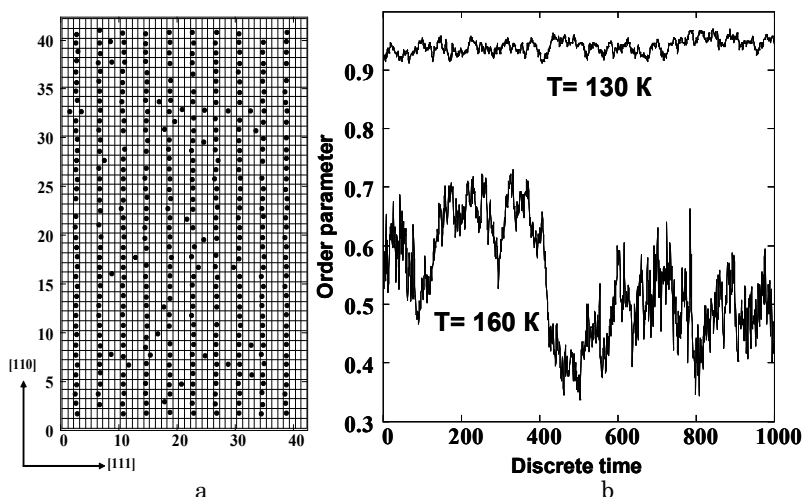
Fig. 1 – The equilibrium adatom structure $p(1 \times 4)$ on the (112) surface of bcc crystal at $\theta = 0.25$ and T = 130 K (a). The order parameter decreases with increasing temperature, but its fluctuations increase (b)
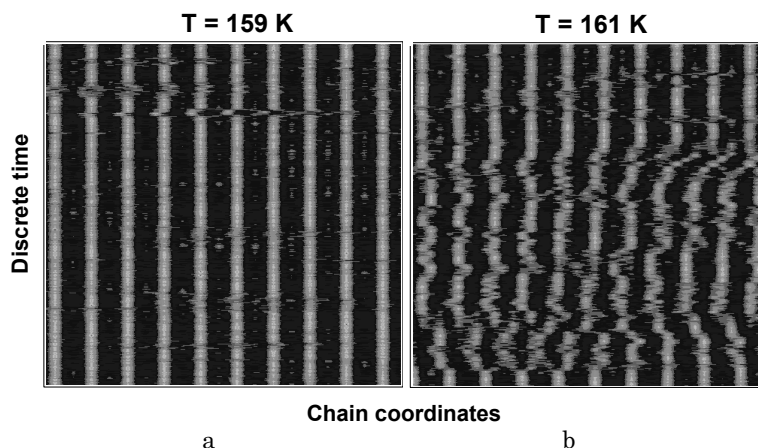
Fig. 2 – At T < T_C, long-range order exists in film and chain coordinates are not changed with time (a). At T > T_C, chain structure becomes incommensurate with the substrate and long-range order changes to quasi-long-range one (b)
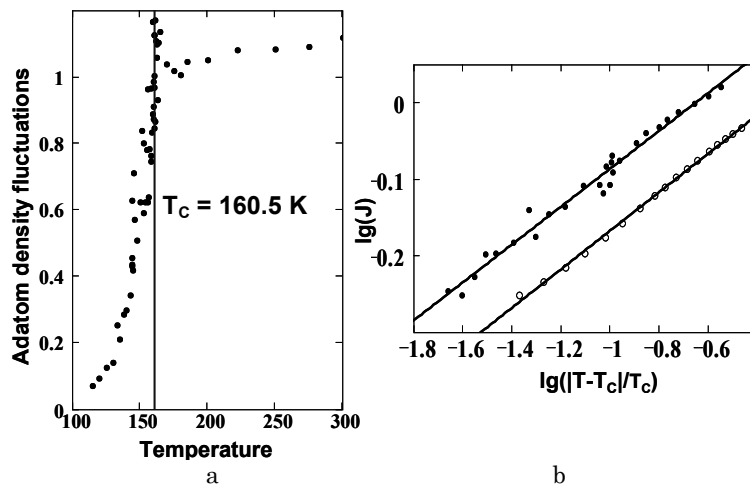
Fig. 3 – A sharp peak is allocated on temperature dependence of adatom density fluctuations along the substrate grooves at the critical temperature (a). The temperature dependences of order parameter in double logarithmic scale for real system Li-W(112) (open circles) and based on the modeling results (filled circles) give almost identical values of order parameter exponents ($\beta \approx 0.25$) (b)

The chains in incommensurate structures begin to move through the crystal in the direction [111]. This means the transition from long-range order to quasi-long one due to temperature depinning of the adsorbed film [5]. The structure of the incommensurate domains remains chain-like at chosen parameters of lateral adatom interactions in the model, but its period becomes 1.1 times shorter than in the p(1 × 4) two-dimensional crystal.

In Fig. 3a, the temperature dependence of the density fluctuations of adatoms is demonstrated. Due to strong anisotropy of lateral adatom interaction, these fluctuations are mainly related to migration adatoms along the grooves.

In the presence of long-range order, there is a translational symmetry with a period four times as large as the substrate lattice constant in direction [111]. The order becomes quasi-long-range after crossing the critical temperature. Chains begin to drift, the average distance between them decreases and the adsorbed film becomes one-dimensionally incommensurate with substrate in [111] direction. At the chosen parameters of lateral adatom interaction, dynamic domain structures p(1×2) or c(2×2) in addition to the incommensurate domain structure are sometimes observed in the film. The life span of these structures amounts to nanoseconds. We can see some signs of a first order phase transition, but mentioned formations are non-equilibrium. The very fact of their existence is only evidence for the temporary structures of fluctuations. Such structuring is a consequence of the random interaction of a part of effectively free adsorbed film with the substrate relief. With increasing temperature, the dynamic chain structure begins to break down, although chains continue to be formed and destroyed, i.e. the many-adatom interaction manifests itself constantly in the process of diffusion. The nature of the interaction varies according to changes in the phase state of adsorbed film with temperature. The values of tracer diffusion coefficients obtained at different temperatures were used to construct the Arrhenius plots. At temperatures below the critical one, the activation energy of diffusion is the highest. The mass transfer is carried out by a kind of vacancy mechanism (see above). At the transition to quasi-long-range order, activation energy of diffusion decreases sharply due to increase of the role of incommensurate chain structures in the diffusion process [5].

The strong changes in diffusion coefficients can be caused by several factors. During the second order phase transition, not only the energy E_d can be significantly changed, but the activation entropy of diffusion ΔS, too [10, 11]. Finally, it is necessary take into consideration that applying the Arrhenius equation to calculate the activation energy and pre-factor (especially in the region of phase transitions) can not be completely justified. The change in temperature can change the system itself (e. g., the degree of order within it or the potential corrugation because of the substrate reconstruction), and not just the probability of overcoming an invariable barrier as it is assumed in the Arrhenius approximation [12, 13]. We obtained the Arrhenius plots with breaks for adsorption systems Sr-W(112) and Sr-Mo(112) [4, 6]. Thus it must be kept in mind that even when such plots can be fairly approximated as linear, the parameters E_d and D_0 derived from them may present only some effective quantities.

In general, surface diffusion is a purely collective (many-particle) phenomenon [13]. Even though we speak about a single atom jump, this event actually involves also a number of surrounding atoms with which the atom interacts more or less intensively. The interaction with them determines the potential barrier height. Owing to the interaction, the atom fluctuatively receives from the substrate and neighboring adatoms, which commonly serve as a thermal reservoir, an excess energy required for overcoming the barrier. After the jump, the adatom returns the excess energy to its surrounding. It does not always fall at once to the bottom of the potential well. In addition, the depth of the well depends on the instantaneous configuration of its environment.

It is important to emphasize the role of Friedel's oscillations in surface diffusion. Just this long-range part of the lateral interaction between adatoms is responsible for the formation of the long-period chain struc-

tures. Choosing our simulation model, we had no quantitative information about the parameters of this interaction. So we did not pose the problem to create a model that would give accurate quantitative values of surface diffusion parameters in addition to qualitative description of real adsorption systems. Thus the depth of the potential minimum caused by electron interference in the direction [111] was rather arbitrarily set to 5 meV. Obviously, the electron density fluctuations should intensify mutually as the atomic chains are formed. This was corroborated experimentally in work [14], where the diffusion of a single copper atom was investigated nearby a specially created chain of copper adatoms and between two parallel chains located at a distance of several tens of Angstroms. The parallel chains formed a quantum resonator in which the amplitude of standing waves greatly increased, causing a diffusion anisotropy due to formation of diffusion channels along the resonator.

In some adsorption systems, such resonators arise spontaneously, resulting in the formation of chain superstructures. Such is indeed the case for some electropositive elements adsorbed on the (112) faces of W and Mo crystals [5]. In their films, the lateral forces have a pronounced long-range character. A sharp increase in their diffusion coefficient occurs at the phase transitions where the commensurability between the film and the substrate is disrupted [5, 13].

4. CONCLUSIONS

Collective effects in surface diffusion play a conspicuous role in submonolayer films adsorbed on the anisotropic atomic surfaces of single crystals. This is due to the strong anisotropy of the substrate atomic structure, which also entails the anisotropy in the lateral interaction of adatoms. At low temperatures, cooperative effects lead to emergence of p(1×N) superstructures, atomic chains in which hinder the easy diffusion of individual atoms along the substrate grooves. With increasing temperature, the diffusion coefficient increases rapidly because of generation of new vacancies and kinks in the chains. When passing through the critical temperature, the domains of a chain-like structure incommensurate with the substrate are formed in the film and the diffusion activation energy decreases sharply. Thermal destruction of the structure p(1 × 4) was found to proceed *via* a second order phase transition which extends over a wide temperature range. The collective effects in surface diffusion of adatoms reveal themselves even at high enough temperatures owing to fluctuative formation and destruction of interacting segments in the adatom chains.

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REFERENCES

1. O.M. Braun, V.K. Medvedev, *Sov. Phys. Usp.* **32**, 328 (1989).
2. A.G. Naumovets, in: *The Chemical Physics of Solid Surfaces*, ed. by D.A. King a. D.P. Woodruff, Elsevier, Amsterdam, **7**, 163 (1994).
3. A.G. Naumovets, M.V. Paliy, Yu.S. Vedula, A.T. Loburets, N.B. Senenko, *Progr. Surf. Sci.* **48**, 59 (1995).
4. A.T. Loburets, N.B. Senenko, A.G. Naumovets and Yu.S. Vedula, *Phys. Low-Dim. Struct.* **10/11**, 49 (1995).
5. I.F. Lyuksyutov, A.G. Naumovets, V.L. Pokrovsky, *Two-dimensional crystals* (Naukova Dumka: 1988).
6. A.T. Loburets, A.G. Naumovets, N.B. Senenko, Yu.S. Vedula, *Zs. Phys. Chemie* **202**, 75 (1997).
7. V.K. Medvedev, A.G. Naumovets, T.P. Smereka, *Surf. Sci.* **34**, 368 (1973).
8. A.T. Loburets, N.B. Senenko, Yu.S. Vedula, A.G. Naumovets, *Ukr. J. Phys.* **50** No 8, 805 (2005).
9. I.F. Lyuksyutov, V.K. Medvedev, I.N. Yakovkin, *Sov. Phys. JETP* **53**, 1284 (1981).
10. T. Ala-Nissila, R. Ferrando, S.C. Ying, *Adv. Phys.* **51**, 949 (2002).
11. H. Loeser, D. Fick, H.J. Jaensch, *J. Phys. Chem. B.* **108**, 14440 (2004).
12. A.G. Naumovets, Z. Zhang, *Surf. Sci.* **500**, 414 (2002).
13. A.G. Naumovets, *Physica A* **357** No 2, 189 (2005).
14. N.N. Negulyaev, V.S. Stepanyuk, L. Niebergall, P. Bruno, W. Hergert, J. Repp, K.-H. Rieder, and G. Meyer, *Phys. Rev. Lett.* **101** No 22, 22660 (2008).