Collective Diffusion Mechanisms in Phase Inhomogeneous adsorbed films

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Introduction

In the case of 2D diffusion, the main physical interest in the phenomenon is that the particles in the diffusion process carry out a complex interaction with each other and the substrate. This leads to a pronounced collective nature of diffusion, sometimes with very specific mechanisms. Adsorbed atoms can form a large number of ordered structures. Their symmetry and thermodynamic characteristics depend on the properties of the particles and the adsorbent and the surface structure, which accordingly affects the diffusion processes [1-5].

The aim of the work is to study the mechanisms of surface diffusion at the atomic level in combination with thermodynamic characteristics (self-diffusion coefficients, activation energy, prefactor in the Arrhenius equation) and the dependences of these parameters on the structure and coverage degree in the first monolayer.

Methods

1. The method of molecular dynamics is used to achieve goal in building a mathematical model of a quasi-one-dimensional 2D system.
2. Changes in the structure of the adsorbed film are accompanied by corresponding changes in the diffusion mechanisms [3, 6, 7]. The peculiarities are found on the isotherms [ln(D(θ)), θ] are used to determine the coverage degrees at which the first order phase transitions occur.
3. The fractures on the Arrhenius graphs are observed due to changes in the activation energy of diffusion at the temperatures of phase transitions. The coordinates of the breakpoints together with the information of point 2 were used to construct the binodal (the line restricting the area of phase coexistence).
4. The frame-by-frame visualization of atoms at different coverages and temperatures was performed for structural analysis, determination of the order parameter, detection of soliton-like configurations.
5. The information about the nature of lateral interaction, derived from experimental work [4, 5, 8] was used when creating a mathematical model. Te following was taken into account:

a) dipole-dipole repulsion;
b) oscillating interaction through the electron gas of the substrate (Friedel oscillations);
c) the proper size of the adsorbed atoms;
d) we did not take into account the processes of metallization and mutual depolarization of atoms in the construction of lateral interaction potentials. It is known that the metallization of the adsorbed films begins at $\theta > 0.5$ [5].

Results

A strong concentration dependence of D(θ) and the presence of specific features on the ln(D(θ)) isotherms (sharp maxima and minima) were revealed. This allowed to establish the region of heterogeneity of the adsorbed film on the [ln(D(θ)), θ] plane, to construct a complete binodal, to find the critical temperature and to estimate the value of the critical coverage θ_C depending on the structural features of the adsorbed film.

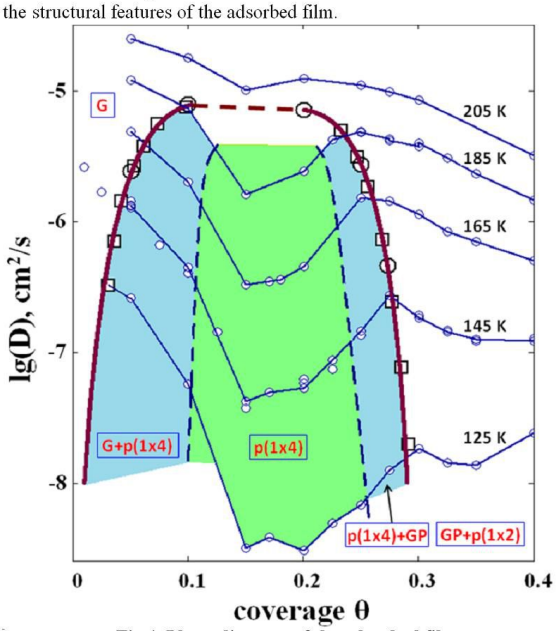

Fig.1. Phase diagram of the adsorbed film

In Fig. 1, isotherms lg(D (θ)) are blue lines and binodal with experimental points is indicated with squares. The points depicted on the binodal by the disks are obtained from Arrhenius graphs. Areas of phase coexistence (the first order phase transitions) are highlighted in blue. In the green area, there is a hexatic phase p(1 × 4), represented by a structure with a large number of vacancies. As θ increases, number of vacancies decreases. Along the burrows of the substrate, the distant order is maintained, but along the chains of adatoms there is only the short one. Islands of disordered (gas) phase begin to appear in the homogeneous structure p(1 × 4) at coverage $\theta \approx 0.25$, i.e. the film becomes heterogeneous.

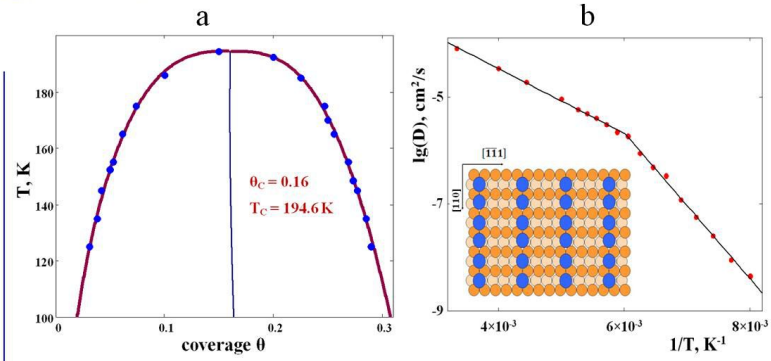

Fig. 2. A binodal constructed in the coordinates (θ, T) (a) and an Arrhenius graph with a model of the structure p(1 × 4) on the face (112) b.c.c. crystal (b)

There is a structure p(1 × 2) to the right of the binodal. It is a crystal at T < 228 K. At higher temperatures, adatoms are able to move freely, constantly changing their neighbors (discrete fluid), despite maintaining a clear periodicity in the adsorbed film. This is shown in Fig. 3.

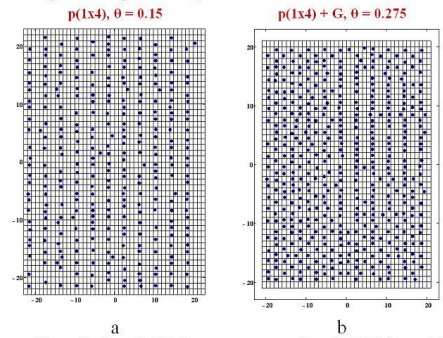

Fig. 3. The structure p(1 × 4), θ = 0.25 for coverages θ = 0.15 (a) and θ = 0.275 (b). If θ = 0.15, the structure contains 40% of vacant centers, located randomly, and the system is homogeneous. Hexatic phase. Diffusion coefficients are minimal. At coverage θ = 0.275, the film decomposes into coexisting islands of structure p(1 × 4) and a denser gas phase. Hexatic phase. Diffusion coefficients are maximum

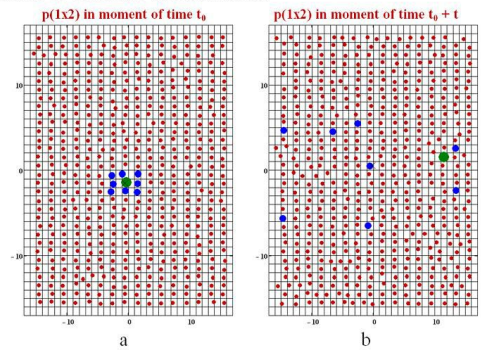

Fig. 4. Stoichiometric structure p (1 × 2), θ = 0.5. The system is homogeneous. Hexatic phase. a - the green disk indicates an arbitrarily selected atom. Eight atoms of its immediate surrounding are marked with blue disks. In the diffusion, the environment of the selected atom is constantly changing, which is characteristic of liquids (b).

Conclusion

The mathematical model, which uses the potentials of lateral interaction constructed on the basis of the results of real experiments, demonstrates the formation of structures p(1 × 4) and p(1 × 2), the presence of which is characteristic of the adsorption systems Li - W(112) and Li - Mo(112). A strong concentration dependence of D(θ) and the presence of specific features on the ln(D(θ)) isotherms (sharp maxima and minima) were revealed. Areas of heterogeneity in the adsorbed film were allocated, a complete binodal was constructed, and a critical temperature and a critical coverage were found. Both structures in the studied temperature range demonstrate the properties of the hexatic phase. The question of the course of diffusion in hexatic phases will be considered in the next work.

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