

Simulation of self-assembling monolayers of complicated organic molecules at the interface

V.F. Fefelov^{*}, V.A. Gorbunov^{*}, A.V. Myshlyavtsev^{*,**}, M.D. Myshlyavtseva^{*}

^{*} Omsk State Technical University, Omsk, Russia, vitaly_gorbunov@mail.ru

^{**} Institute of Hydrocarbons Processing SB RAS, Omsk, Russia

ABSTRACT

In present paper we construct and study the general model of self-assembling monolayer (SAM) of complicated organic molecules and investigate three special cases of this model. All models were investigated with grand canonical ensemble Monte Carlo method and transfer-matrix technique. The simplest general model elaborated for SAMs shows rich phase diagram analogous to that for real SAMs; the structures of the model ordered phases are also analogous to the structures of SAMs; for SAMs the non-monotonous dependence of the total coverage on the pressure is possible, i.e. at the increase of pressure the empty surface area can grow that can take some effect on physicochemical processes on surface.

Keywords: self-assembling monolayer, adsorption, Monte Carlo, transfer-matrix, adsorption state

1 INTRODUCTION

The progress in modern micro- and nanoelectronics results from the transition to qualitatively new level of development – the level of atoms, molecules and its ensembles. Concerning this aspect a self-assembled monolayers consisted with complex organic molecules (organic SAM) are one of the most perspective. The organic SAMs have a numerous applications for field effect transistors, light-emitting diodes, nonlinear optics, gas sensing and even molecular-based information storage [1,2]. In this devices the structure of organic SAM is crucial as the template for growth of the bulk film influencing the grain structure, orientation, and even the polytype of the organic layer.

The self-assembly of organic supramolecular nanostructures is based on noncovalent interactions between the adsorbate–adsorbate. These interactions include the van der Waals interactions, hydrogen bonding, electrostatic interactions or weak donor–acceptor interactions, dipole–dipole interactions, hydrophobic interactions and π – π stacking and others [2-4]. However, molecular self-assembly on solid surfaces is more complicated process involving a balance between the adsorbate–adsorbate and adsorbate–substrate interactions. Naturally these interactions depend on both geometry and chemical properties of an adsorbate molecule and morphology as well as physicochemical properties of a

substrate. Strength of the adsorbate–substrate interactions and morphology of surface influence molecular surface mobility and therefore plays a key role in the formation processes of the self-assembled structures. Very interesting features of organic SAMs are multisite adsorbate–substrate interactions and ability of molecules to have different orientations with respect to the interface. The possible orientation depends on concentration, pressure, temperature, surface electric potential and other parameters [1,2,5,6]. It is worth to note that there are the ordered structures which contain the molecules with two different orientations [1,7,8]. Existence of several molecule orientations with respect to the interface results in the dependence of the average interface area per molecule on the pressure or other parameters.

To date, the most of theoretical studies concerning of the behavior of complicated organic molecules at interface are devoted to quantum-chemistry investigation of one or few organic molecules adsorbed on small clusters of metals. There is no still a general model of organic SAMs on the interfaces which allows us to predict the macrostructure and thermodynamic properties of whole SAMs depending on the geometry and chemical structure of molecule and substrate. Therefore, the goal of presented work is to construct and study the simplest general organic SAMs model taking into account the different orientation of adsorbate.

2 MODEL

It is well known that a lattice gas model is a good approximation for adsorption process. We consider the one as the organic SAMs model. The simplest model which takes into account the possibility of different orientation of adsorbed molecule with respect to the surface is the known model of homonuclear dimers adsorption [9]. In this model it is assumed that molecules can adsorb parallel or perpendicular to the surface occupying two or one adsorption sites, respectively. Let us to generalize the model of dimer adsorption and following [10] introduce the general model for complicated molecules adsorption. We assume the molecule can be adsorbed on the surface by the k ways occupying the m_1, m_2, \dots, m_k active centers located in the corresponding configurations on homogeneous or heterogeneous lattice, respectively. Further we describe the three simplest (not counting the described model of the dimer adsorption) special cases of the general model.

2.1 The simplest model of complicated molecules adsorption on the square lattice

We consider the homogeneous square lattice of $M = L \times L$ size with periodic boundary conditions as the surface model and assume that the molecules can be adsorbed by only two different ways. At the first way the molecule occupies the one active center and at the second way the molecule gets the four ones. These four centers form the square. Thus, for this model we have $k = 2, m_1 = 1, m_2 = 4$. We assume that a nearest neighborhood between two adsorbed molecules (independently of the adsorption way) is prohibited. The allowed configurations of the adsorbed particles are schematically shown in Fig. 1. The difference between the heats of adsorption of the four-center location and the mono-center one is noted as Δ .

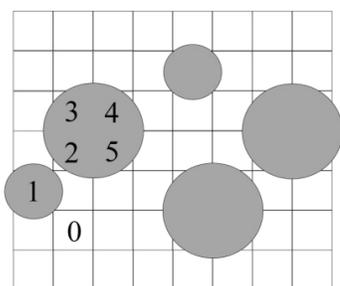


Figure 1: Allowed configurations of adsorbed particles [10].

Thermodynamic Hamiltonian for the system under consideration can be written as

$$H = -\frac{\Delta}{4} \sum_i n_i - \mu \left(\frac{1}{4} \sum_i n_i + \sum_i c_i \right) \quad (1)$$

where c_i and n_i are occupation variables, and c_i equals to 1 if given site occupied by segment of the molecule adsorbed on one site, and n_i equals to 1 when given site occupied by segment of the molecule adsorbed on four sites; c_i and n_i equal zero if given site is empty; $\Delta = h_2 - h_1$ is the difference between heats of adsorption on four sites (h_2) and one site (h_1); μ is chemical potential.

This model we constructed to understand the influence of different adsorbate orientation on properties of organic adlayer. Let us call this model "Model 1".

2.2 The simplest model of complicated molecule adsorption on the stepped surface

This model is constructed to investigate the influence of surface heterogeneity on structure and features of the adlayer, which consists of complicated molecules with different orientations. The heterogeneous surface in the model is represented as the stepped surface. This is a

natural state of high Miller's index planes of single metal crystals.

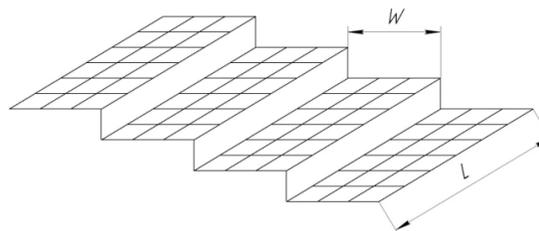


Figure 2: Model of stepped surface [11].

The model is the same to previous one but as the surface model we use the stepped surface [11]. The model of stepped surface is represented as two-dimensional square lattice with size $M = L [W \cdot n]$, where L – length of step, W – width of step and N – amount of steps (Fig. 2). Let us call this model "Model 2". In this model we suppose that all sites are energy-wise equivalent. But even in this case sites do not all are equivalent in general. We consider in this model that molecules adsorbed on neighbor sites of different steps either interact or do not interact according to orientation of molecule adsorbed on lower step. When molecule adsorbed on one site of lower step there is prohibited adsorption on the nearest-neighbor site of higher step (Fig. 3c and Fig. 3d). Also adsorbed molecules cannot be located on two different steps simultaneously (Fig. 3e).

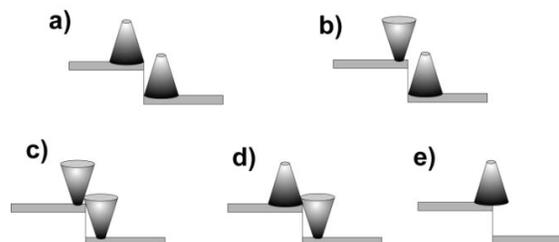


Figure 3: Configurations of adsorbed molecules. a, b) configurations are allowed; c, d, e) are prohibited [11].

2.3 The model of adsorption of unsaturated cyclic hydrocarbons on reconstructed surface Si(001)

This model illustrates how our general model can be used to describe the adsorption of specified molecules by example of unsaturated cyclic hydrocarbons on the surface of semiconductors.

Silicon (001) surface is reconstructed in such way that adjacent Si atoms pair together into dimers Si=Si which arrange into rows forming the structure (2x1) as it is shown in. In terms of lattice gas model this surface can be represented as two-dimensional lattice of square symmetry in which active sites form (3x1) structure.

Adsorption of unsaturated organic molecule on the Si(001)-2×1 surface goes through the reaction of [2+2] cycloaddition with formation of di-σ bond Si-C. When hydrocarbon molecule has more than one unsaturated bond then it is able to have several configurations on the surface depending on the number of di-σ bond Si-C.

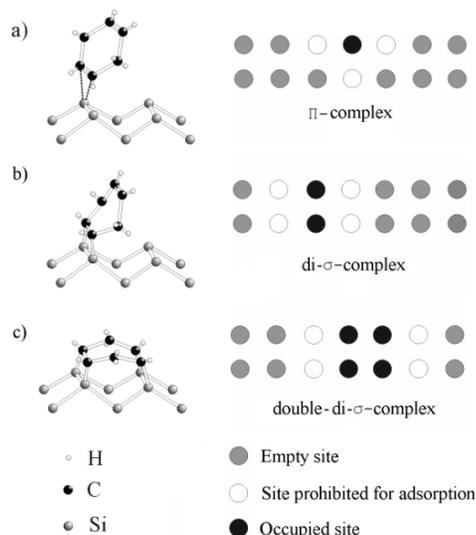


Figure 4: Schematic adsorption models of 1,4-cyclohexadien on Si(001) surface [8].

To study the adsorption of unsaturated cyclic hydrocarbons on reconstructed Si(001) surface we chose 1,4-cyclohexadien because as experiments show depending on the conditions this simple molecule can adsorb by three ways [8]: (i) intact molecular adsorption (π -complex; Fig. 4a), (ii) single di-σ bonding adsorption (Fig. 4b), and (iii) double di-σ bonding adsorption (Fig. 4c). In the framework of lattice gas model these adsorption complexes can be represented as it is shown on the Fig. 4.

Each of these adsorption complexes has its own heat of formation: Δ_1 for di-σ complex and Δ_2 for double-di-σ complex. Heat of formation of π -complex we took into account implicitly in chemical potential μ . In order to decrease the number of model parameters we assumed that heat of formation of double-di-σ complex twice as much as

it for di-σ complex, thus $\Delta_1 = \Delta$ and $\Delta_2 = 2\Delta$.

To a first approximation we assume that a nearest neighborhood between two adsorbed molecules (independently of the adsorption way) is prohibited. Due to the own size of the molecule is less than distance between neighbor rows of Si=Si dimers then the interactions between molecules adsorbed on neighbor Si=Si rows can be neglected. This fact allows us without loss of generality to consider adsorption only on one row of Si=Si dimers. Thus, Si(001) surface can be represented as two-dimensional $M=2 \times L$ array of sites. Let us call the constructed model – “Model 3”.

Thermodynamic Hamiltonian for this model can be written as

$$H = -\mu \left(\sum_i c_i + \frac{1}{2} \sum_i n_i + \frac{1}{4} \sum_i m_i \right) - \frac{\Delta}{2} \left(\sum_i n_i + \sum_i m_i \right) \quad (2)$$

where c_i , n_i and m_i are occupation variables, and c_i equals to 1 if given site is a part of π -complex, n_i equals to 1 when given site is a part of di-σ complex, and m_i equals to 1 when given site is a part of double-di-σ complex; c_i , n_i and m_i equal zero if given site is empty.

3 RESULTS AND CONCLUSIONS

To study all the constructed models we used two well-known approaches: Monte Carlo [12] and transfer-matrix techniques [13,14], which complement each other well. In particular, such values as entropy are calculated much simpler by transfer-matrix method than by Monte Carlo method. All models were investigated in the grand canonical ensemble.

For all models we calculated as simple averages a number of thermodynamic quantities such as: isotherm $\rho(\mu)$ (dependence of relative number of adsorbed molecules on chemical potential); coverage $\theta(\mu)$ (dependence of relative number of occupied sites on chemical potential); partial isotherms and coverages (relative number of molecules adsorbed in particular way or relative number of sites occupied by molecules adsorbed in particular way, respectively); internal energy and differential heat of adsorption.

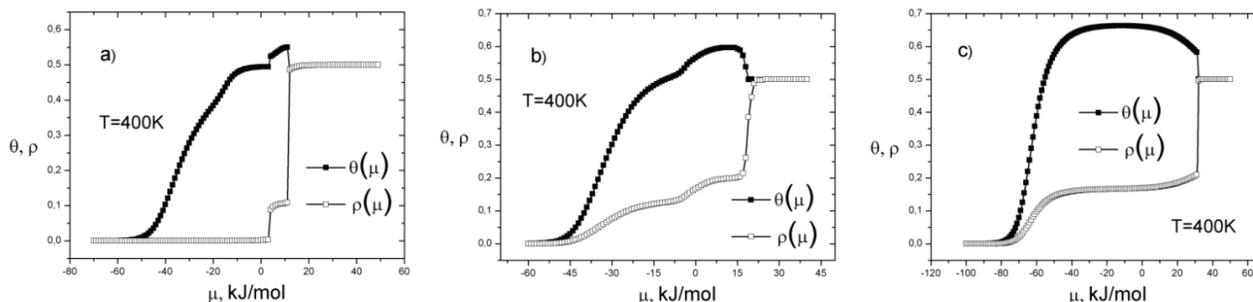


Figure 5: Typical coverage $\theta(\mu)$ dependences on chemical potential and isotherms $\rho(\mu)$ for: a) Model 1; b) Model 2; and c) Model 3.

Based on obtained results we can do the number of general conclusions which are true for all investigated models.

For organic SAMs the non-monotonous dependence of the total coverage on the chemical potential is possible, i.e. at the increase of gas phase pressure the empty surface area can grow. However, isotherms, as it follows from general thermodynamic laws, are monotonous increasing functions (Fig. 5). This phenomenon can take some effect on physicochemical processes on surface. And we suppose that this qualitative feature peculiar to the studied models takes place in the majority of the more realistic models describing formation of self-assembling monolayers of complex organic molecules.

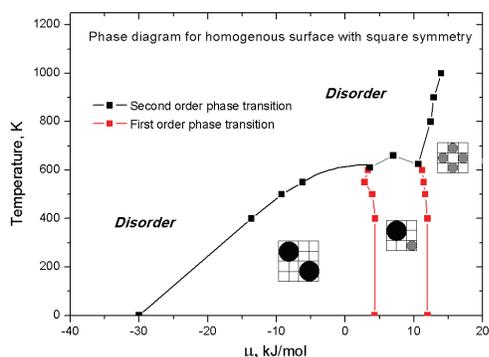


Figure 6: Phase diagram for organic SAM on homogenous square lattice calculated with our Model 1

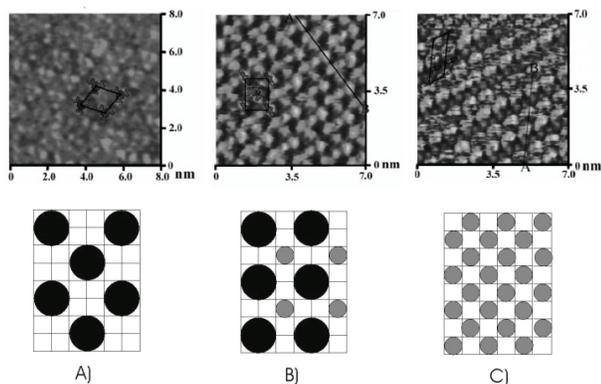


Figure 7: Structures of real SAM of trimesic acid on Au(111) investigated by in situ scanning tunneling microscopy [1] (top of the Figure) and corresponded structures of SAM appeared in Model 1 (at the bottom of the Figure).

The modern methods of theoretical physics such as the multiple-histogram reweighting and finite scaling techniques (the fourth-order cumulant of the order parameter) have been used to estimate the phase diagram of complicated organic molecules adsorbed on the homogenous square lattice (Model 1). We can conclude that the simplest model elaborated for SAMs shows rich phase

diagram analogous to that for real SAMs (Fig. 6). The structures of the model ordered phases are also analogous to the structures of SAMs (Fig. 7).

Investigating the adsorption of complicated organic molecules on heterogeneous surface we focused on the most interesting case when the steps width commensurable with the adsorbate size. And we can conclude that stepped surface heterogeneity can lead to a wide variety of ordered surface structures many of which are not observed formerly in the study of adsorption of such molecules on the homogenous surface. It was shown that the surface heterogeneity can define primary molecule orientation, macrostructure of adlayer and even existence of long-range order in the organic SAM.

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