

---

Proceedings of the 12th International Symposium UFPS, Vilnius, Lithuania 2004

## Modelling of SubPc Self-Assembly on Ag(111)

V. PETRAUSKAS<sup>a,\*</sup>, E.E. TORNAU<sup>a</sup> AND S. LAPINSKAS<sup>b</sup>

<sup>a</sup>Semiconductor Physics Institute, 2600 Goštauto 11, Vilnius, Lithuania

<sup>b</sup>Faculty of Physics, Vilnius University, 2054 Saulėtekio 9, Vilnius, Lithuania

The ordering of subphthalocyanine molecules into honeycomb and hexagonal close packed patterns on Ag(111) is described using complex Lennard–Jones-type intermolecular potential. We rescale Ag(111) lattice, and take into account an infinite exclusion of first, second, and third neighbours, attraction — of fourth and fifth, and repulsion — of sixth and seventh. The phase diagram is obtained by the lattice gas model using Monte Carlo simulations. Very strong first order phase transitions, causing the two-phase co-existence, are found between disordered and honeycomb as well as between disordered and hexagonal closed packed phases.

PACS numbers: 64.60.Cn, 68.43.Hn, 79.60.Dp, 81.07.Nb

### 1. Introduction

Organic molecules on metal surfaces, prepared using, so-called, “bottom-up” technologies or self-assembling, are currently studied as prototypes of possible single molecule memory devices. Subphthalocyanines, well-known as dye materials with high non-linear optical sensitivity, are just one group of such molecules. Their derivative, chloro(subphthalocyaninato) boron(III) (SubPc), schematically has the form of three-lobed wind-blown umbrella with boron-chlorine axis serving as a handle [1]. Adsorbed on metal surfaces, such as Ag or Au(111), SubPc shows a variety of self-assemblies at room temperature. E.g. ordered honeycomb and hexagonal closed packed (hcp) patterns are found in SubPc/Ag(111), but always in co-existence with 2D lattice gas [2, 3].

The modelling of ordering in SubPc/Ag(111) system is quite challenging from the point of view of phase transition theory. The SubPc molecules are very large, SubPc/Ag(111) system has interesting rotational symmetry, and the ordering depends on mutual arrangement of neighbouring molecules. All ordered SubPc structures on Ag(111) were observed by STM at room temperature. Therefore, there is an obvious need for the phase diagram, predicting the behaviour of SubPc/Ag(111) system in all range of temperatures and molecule concentrations. To calculate the

---

\*corresponding author; e-mail: vytas@pfi.lt

phase diagram of SubPc/Ag(111) we first propose the intermolecular potential and then employ the lattice-gas model and use Monte Carlo (Metropolis algorithm) simulation.

## 2. Model

The exact position of SubPc molecule on Ag(111) is not determined as yet. The choice between the intersite and “on-top” position is the choice between 3- and 6-fold symmetry of the adsorption site. There are several reasons to prefer the intersite as the rest point of the SubPc molecule: (i) semi-empirical electron density functional computations [4], (ii) geometrical considerations when arranging the SubPc molecules in honeycomb and hcp patterns according to experimentally found [3] intermolecular distances and angles (see Fig. 1), (iii) some simplification of the model, since for 3-fold case the lowest-energy orientation of the adsorbed molecule is uniquely defined by its location provided the following procedure is done: one has to discriminate between two limiting 3-fold geometries of SubPc on Ag(111): the legs of SubPc “triangle” can point towards intersites or towards centres of the nearest Ag atoms. We have assumed the former orientation as the lower energy state.

Intermolecular interactions (including also intermolecular interactions via the surface),  $J(R_{ij})$ , determine the distance between two molecules and define the symmetry of the ordering. Redistribution of SubPc and Ag electrons can modify the corrugation of the surface potential for SubPc molecules and lead to oscillatory interaction energy with more complicated dependence on separation distance. We assume (using analogy with the STM studies of Co and Cu on Cu(111) [5]) that  $J(R_{ij})$  is described by a Lennard–Jones-type potential which depends on  $R$  starting from repulsion to attraction and repulsion again. Thus in our model  $J(R_{ij})$  is a superposition of (i) very strong exclusion in several first coordination spheres (due to the fact that the size of SubPc  $\gg a_{\text{Ag}}$ ), (ii) Coulomb or van der Waals attraction outside the sphere of exclusion (the attractive interactions are usually responsible for aggregation of particles into islands of different density and occurrence of phase-coexistence) and (iii) repulsive dipole–dipole forces, since SubPc molecules have uniaxial dipole moments. The minimum of this potential,  $J(R_{ij}) = J_k$ , corresponds to the intermolecular distance (measured in number of coordination spheres of Ag(111)) obtained for the honeycomb structure. Thus to describe the SubPc ordering on Ag(111) we propose the lattice-gas Hamiltonian

$$H = \sum_{ij} J(R_{ij})n_i n_j - \mu \sum_i n_i. \quad (1)$$

Here the summation is over the intersites of triangular lattice of Ag(111), the occupation number  $n_i = 1$  if the intersite is occupied by the centre of the molecule and 0 if it is empty, and  $\mu$  is the chemical potential.

Evaluation of intermolecular distances, at which the honeycomb and hcp structures were observed [3] at room temperature, demonstrated that they corre-

spond to  $k_{\text{hon}} = 29$  and  $k_{\text{hcp}} = 36$  coordination spheres. Such long distances make the solution of our model quite complicated, because one has to sort out all necessary contributions to the Hamiltonian up to such distances. We, however, noticed that honeycomb and hcp structures could be realized as the ground states of our model for some other values of  $k$ , e.g. for  $k_{\text{hon}} = 4$  and  $k_{\text{hcp}} = 5$ , if the Ag(111) lattice is rescaled as shown in Fig. 1. For the reduced model for simplicity we approximated the potential by the solid-line in Fig. 2a.

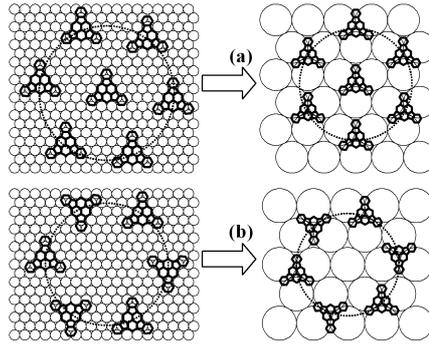


Fig. 1. Rescaling of the model with  $k_{\text{hcp}} = 36$  and  $k_{\text{hon}} = 29$ , proposed in STM experiments [3], to our model with  $k_{\text{hcp}} = 5$  and  $k_{\text{hon}} = 4$ : (a) hcp phase; (b) honeycomb phase.

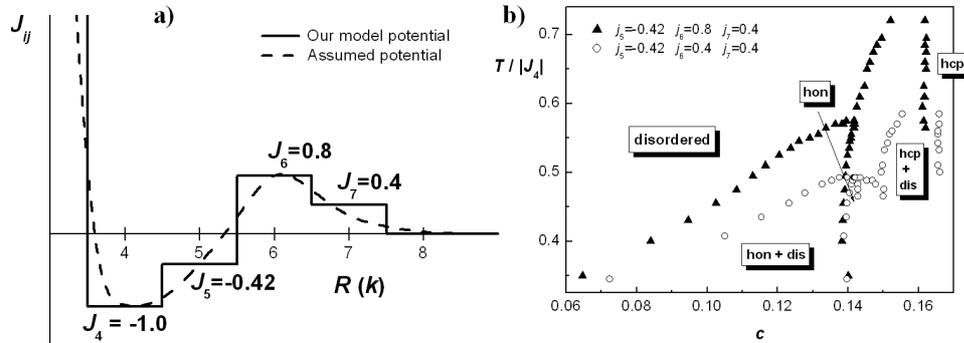


Fig. 2. (a) Intermolecular potential (dashed line) and its approximation by our model (solid line). Distance is expressed in number of coordination spheres of triangular lattice. (b) Phase  $(T/|J_4|, c)$  diagrams obtained for  $42 \times 42$  lattice for  $j_5 = -0.42$  and two different sets of interaction constants:  $j_6 = 0.4$  and  $j_7 = 0.4$  (circles) and  $j_6 = 0.8$  and  $j_7 = 0.4$  (triangles). The SubPc concentration of a pure honeycomb phase  $c = 1/7$  corresponds to experimental [3] packing density of 0.24 molecules/nm<sup>2</sup> and  $c = 1/6$  of a pure hcp phase corresponds to that of 0.34 molecules/nm<sup>2</sup>.

### 3. Results

For our Monte Carlo calculations we used triangular lattice with  $42 \times 42$  Ag atoms with periodic boundary conditions. We used Metropolis algorithm and Glauber dynamics (fixed chemical potential) for  $j_5 = -0.42$  and several sets of interaction constants with different dipole repulsion  $j_6 = 0.4$  (and 0.8) and  $j_7 = 0.4$  (and 0.2). Here  $j_i = J_i/|J_4|$ . The number of MCS/site to reach the equilibrium were around  $10^5$  for transitions to both ordered phases.

The obtained  $(T/|J_4|, c)$  diagrams are presented in Fig. 2b. We determined the phase transition points,  $T_c$ 's, between disordered and ordered phases by calculating temperature dependences of specific heat and SubPc molecules concentration,  $c$ , at a fixed value of  $\mu$ . In the vicinity of the phase transition both dependences demonstrated well-expressed hysteresis implying first-order phase transitions between the phases (phase separation) caused by strong attractive interaction at intermediate distances. The magnitude of this attraction as well as the magnitudes of other interactions are unavailable at the moment. Still we can conclude that with an increase of repulsive forces in the system: (i) the values of the phase transition temperature  $T_c$  increase, and especially  $T_c$  of disordered-to-hcp phase; (ii) the maximum of the honeycomb phase in  $(T/|J_4|, \mu)$  diagram (not shown here) moves from  $\mu = -0.2$  ( $j_6 = 0.4$ ,  $j_7 = 0.2$ ) to  $\mu = 0$  ( $j_6 = 0.8$ ,  $j_7 = 0.4$ ). The area, where the honeycomb and disordered phases co-exist in phase diagram at  $c > 1/7$  correspondingly narrows and disappears for  $j_6 = 0.8$ ,  $j_7 = 0.4$  due to the vicinity of the honeycomb-to-hcp phase boundary; (iii) the vanishing of this co-existence increases the area, where hcp and disordered phases co-exist.

In summary, all obtained results strongly corroborate the conclusions of STM studies [2, 3]: honeycomb and hcp phases mostly co-exist with disordered phase, and pure ordered phases are found only around their stoichiometric concentrations.

We thank EC project PRAMA for financial support.

### References

- [1] A. Meller, A. Ossko, *Monatsh. Chem.* **103**, 150 (1972).
- [2] S. Berner, M. Brunner, L. Ramoino, H. Suzuki, H.-J. Guentherodt, T.A. Jung, *Chem. Phys. Lett.* **348**, 175 (2001).
- [3] S. Berner, M. de Wild, L. Ramoino, S. Ivan, A. Barratoff, H.-J. Guentherodt, H. Suzuki, D. Schlettwein, T.A. Jung, *Phys. Rev. B* **68**, 115410 (2003).
- [4] A. Alkauskas, A. Baratoff, C. Bruder, *ECOSS22 Abstracts*, Prague 2003, p. 17004.
- [5] N. Knorr, H. Brune, M. Epple, A. Hirstein, M.A. Schneider, K. Kern, *Phys. Rev. B* **65**, 115420 (2002).