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Modeling of Surface Diffusion for Stepped Surfaces: Transfer Matrix Approach

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1. Introduction

Surface diffusion is of considerable intrinsic interest and also important for understanding the mechanism of surface reactions [1,2]. It is well known that diffusion of chemisorbed particles occurs, as a rule, via jumps between nearest- neighbor sites and can be rather accurately described in the frameworks of the transitient state theory and lattice-gas model. For simplicity we assume that the tops of diffusion potential barriers are the same for all lattice sites. In this case, the chemical diffusion coefficient can be expressed as

$$D(\theta) = D(0)\exp(\mu / RT)\frac{1}{RT}\frac{\partial\mu}{\partial\theta}P_{00}, \qquad (1)$$

where *D(0)* is the chemical diffusion coefficient at the low coverage, μ is the chemical potential of adparticles, *R* the universal gas constant, *T* the absolute temperature in K, θ the surface coverage, P_{00} the probability to find an empty couple of the nearest neighbor site [2]. To calculate the chemical diffusion coefficient the cluster approximation [1] or Monte Carlo simulation [2] are usually employed. It was shown that this problem can be also solved by the transfer matrix technique [3]. In this paper we employ the latter approach for study of the simplest model of stepped surface.

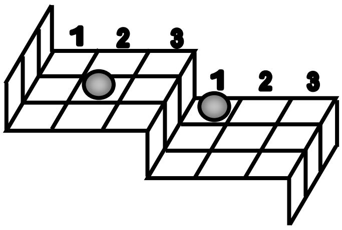

Fig. 1: The model of surface.

2. Model of surface and results

The simplest model of stepped surface was considered in [4]. This model is shown in Fig. 1. The width of terraces is noted as *L*. We assume that adsorption sites belonging to each first row are represented by a potential well with the depth Δ. We take into account the nearest – neighbor lateral interactions as well. The Hamiltonian for the developed model can be written as

$$H = \varepsilon\sum_{<nn>} n_i n_j - \mu\sum_{i} n_i - \Delta\sum_{k} n_k , \qquad (2)$$

where ε is the lateral interaction energy, n_i the occupation number for *i*th lattice site. Here, <*nn*> means summation over all pairs of the nearest lattice sites. In the second term one takes the summation over all lattice sites. In the third term one takes the summation over the sites belonging to the first rows (the rows are oriented along the *X* axis).

As the model under consideration is anisotropic the probability P_{00} is also anisotropic. In this case we should use the following equations

$$H = \varepsilon_x \sum_{<nn>_x} n_i n_j + \varepsilon_y \sum_{<nn>_y} n_i n_j - \mu \sum_i n_i - \Delta \sum_k n_k \,, \tag{3}$$

$$P_{00,x} = 1 + \frac{1}{RT} \frac{\partial \Omega}{\partial \varepsilon_x} - 2\theta \,, \tag{4}$$

where Ω is the grand thermodynamic potential. It has been calculated by the transfer matrix method. Thus the equations (1), (4) allow to obtain the coverage dependence of the chemical diffusion coefficient for the simplest model of stepped surface. The obtained results are shown in Fig. 2. The upper curves from each pair correspond to the *X* axis. The main feature is the independence of the anisotropy of the chemical diffusion coefficient at large coverage from the ratio Δ/ε. Notice, that for the special case *L* = 2 this anisotropy has strong dependence on the ratio Δ/ε.

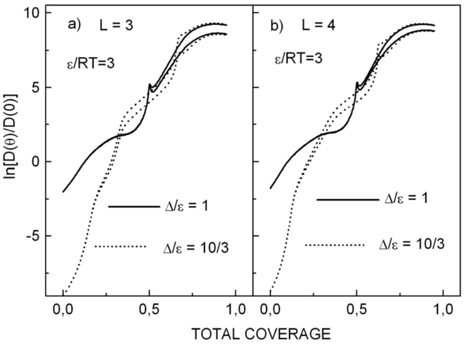

Fig. 2: Chemical diffusion coefficient

3. Conclusion

1. The transfer matrix method is an efficient tool in studying of the chemical diffusion for heterogeneous lattice models with 2D-translational groups.
2. It was shown in the framework of the model under consideration that the chemical diffusion coefficient is essentially anisotropic at large surface coverage.
3. It was shown that for *L* = 2 the chemical diffusion coefficient anisotropy has strong dependency on the ratio Δ/ε and the one is independent from this ratio for *L* ≥ 3.

References

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