SURFACE PHYSICS
AND THIN FILMS

Quantum Mechanical Approach for Determining the Activation Energy of Surface Diffusion

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Abstract—A quantum mechanical approach was proposed to determine the activation energy of surface diffusion for copper, nickel, zinc and iron atoms adsorbed on a copper substrate during electrocrystallization for various overvoltages of the substrate. The activation energy of surface diffusion was calculated from the crystal total energy. An increase in the activation energy of surface diffusion with increasing surface potential is associated with an increase in the binding energy between the ad-atom and the substrate.

1. INTRODUCTION

Surface diffusion consisting in mass transfer over the surface of a solid is one of the important stages in many surface processes, especially during electrocrystallization [1].

The electrode surface, over which surface diffusion occurs during electrocrystallization, is an equipotential surface, and the driving force of such a process is not only thermal motion, but also an excess energy of the ad-atom.

Diffusion over a metal surface largely depends on the surface structure [2]. A real crystal has an inhomogeneous surface and is characterized by a complex microrelief. In real conditions, the surface contains many foreign atoms that have adsorbed or emerged from the solid phase.

The activation energy (E_S) is the most important parameter for surface diffusion. There are various methods for the experimental study of surface diffusion, which detect the particle displacement (labeled atoms, determination of work function).

In order to determine the activation energy, it is necessary to know the surface energy relief of the "substrate–ad-atom" system. Therefore, calculating E_S is extremely difficult. As of now, the most popular theoretical method for calculating E_S for metals is the embedded atom method (EAM) [3] and cohesive approximation. In [4], an approach to the determination of the activation energy of surface diffusion, which is based on the cohesive approximation to the calculation of the adsorption properties of atoms, was proposed. It was shown that calculated E_S for diffusion of atoms of all transition metals, as well as rare-earth

metals, over the surface of crystalline plane (110) of tungsten correlate with measured values.

In this work, we present the results of theoretical calculations of the activation energy of surface diffusion, which are based on the cohesive approximation, for copper, nickel, zinc, and iron atoms adsorbed on a copper substrate during electrocrystallization.

2. MODELS AND CALCULATION METHODS

Let us to consider the motion of an ad-atom on the crystalline surface of the substrate. We represent the surface as a periodic set of adsorbed positions, which correspond to the positions of energy minima. Surface diffusion can be considered as a jump from one surface cell to an adjacent one [5, 6]. We assume that during jumping from one surface cell to another (adjacent one), the length of the adsorption bond remains unchanged.

The surface diffusion upon electrocrystallization is considered as the movement of the ad-atom of the deposited metal over the substrate surface, in which the ad-atom position changes from one crystal lattice site to another through equal distances.

Consider the surface diffusion of nickel and copper ad-atoms with a fcc structure over the substrate. At the initial stages of crystallization and during the growth of films, the substrate has no growth steps.

Figure 1 shows the surface of a fcc crystal ((100) plane). The ad-atom is located at the crystal lattice site A in the (200) plane at a distance of $0.5a$ (a is the crystal lattice parameter).
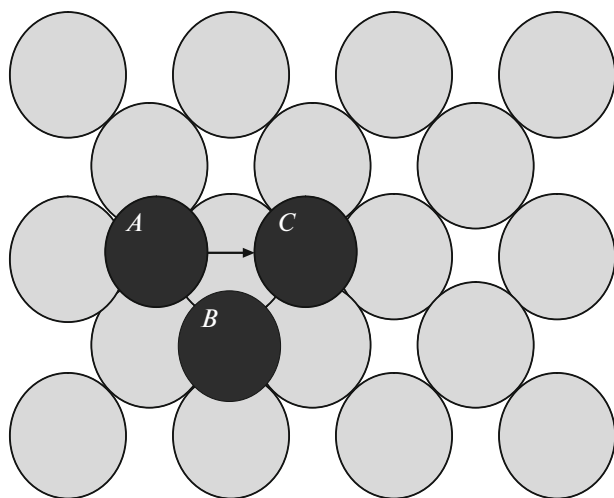
Fig. 1. Schematic of diffusion of ad-atom over the surface of fcc crystal in (100) plane: *A* is the initial position, *B* and *C* are the final positions.

The diffusion of the ad-atom into the nearest position *B* is possible. The jumping length between the sites *A* and *B* is $b = a\sqrt{0.5}$. It is also possible to move between the sites *AQ* and *C* with a jumping length $b = a$.

In order to determine the activation energy, we calculated the total energy of the substrate with ad-atom in each of these positions as differentiated from cohesive approximation. In this case, the geometric model of a crystal with ad-atom, in which the number of atoms in the crystal structure was selected by recognizing that the ad-atom has to interact with substrate atoms in at least five coordination spheres, was constructed. Consequently, the activation energy of surface diffusion will be determined as the difference between the total energies of the crystal with ad-atom in the equilibrium adsorbed state with minimum energy (W_{min}) and in the transitional saddle point characterized by maximum energy (W_{max}) [7]:

$$E_S = W_{max} - W_{min}. \quad (1)$$

The total energy of the crystal with adsorbed atoms was calculated using one of the most widespread methods to investigate electronic structures of atoms, molecules, clusters, solids, etc.—the density functional theory (DFT) [8, 9]. The DFT results are highly accuracy just as the results of ab initio methods of accounting for electron correlation. This theory imposes moderate demands on computational resources, which make it possible to carry out the calculations of systems consisting of hundreds of atoms and interesting for modern nanotechnology [10].

In addition, the DFT is used to study the adsorption characteristics of transition metals [11−13], in this work, their kinetics of electrocrystallization is studied.

According to the DFT, the total energy (*W*) is determined by the following expression

$$W = U - \frac{1}{2}\sum_{i=1}^{N_{occup}}\int \phi_i^*(r)\nabla^2\phi_i(r)dr - \sum_K \int \frac{\rho(r)}{|r - R_K|}dr$$
$$+ \frac{1}{2}\int\int \frac{\rho(r)\rho(r')}{|r - r'|}drdr' + E_{XC}[\rho], \quad (2)$$

where Z_K and R_K are the charge and spatial coordinates of an immobile *K*-th nucleus, respectively, and the electron density determining by the formula

$$\rho(r) = \sum_{i=1}^{N_{occup}}|\varphi_i(r)|^2, \quad (3)$$

where $\varphi_i(r)$ is the one-electron Kohn−Sham (molecular) orbital.

Equation (2) takes the following form:

$$W = U + T_S\{\phi_i(r)\}_{i=1}^{N_{occup}} + V_{ne}[\rho] + J[\rho] + E_{XC}[\rho], \quad (4)$$

where *U* is the potential energy of interaction between the nuclei, T_S is the electron kinetic energy, V_{ne} is the attraction of electrons to nuclei, *J* is the classical contribution to the energy of interelectronic repulsion, and E_{xc} is the exchange-correlation functional including static electron correlation.

Numerous studies of characteristics of molecules and clusters by the DFT [14−16] showed good results in correct deciding on the exchange-correlation functional. It was shown in [17, 18] that the most suitable functional for calculating the structural and thermochemical characteristics of metal complexes is the three-parameter hybrid functional B3LYP [19−21]. It is also known that the use of hybrid exchange-correlation functionals in the DFT makes it possible to successfully calculate the structural and electronic characteristics of complexes of transition and heavy metals with reasonable consumption of computer time [22−25].

There is a number of review and original works devoted to the determination of functional type that allows to calculate the characteristics of transition metals with high accuracy [26−33]. The structural characteristics of transition metals, which are calculated using B3LYP functional, was shown to have the accuracy just as in the ab initio methods.

The selection of hybrid functional B3LYP is justified by the tests of exchange-correlation functional M062X and hybrid functional B3LYP and PBE1PBE [7].

Furthermore, it is necessary to take into account that the difference values between the energies rather than absolute values of energies are used for calculating binding energies and determining the activation energies of surface diffusion.

Energy values were calculated for metals, for which the interaction between the valence electrons plays an
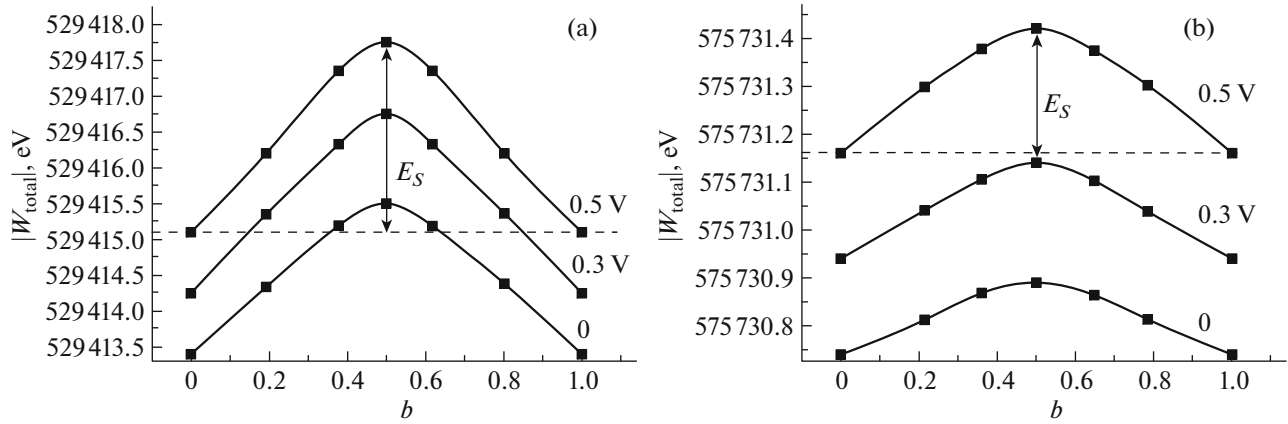
Fig. 2. The values of total energy (W) for copper crystal as a function of length of jump (b) of ad-atom diffusing from position A into (a) B and (b) C.

important role. This principle was used to select the basis set. To describe such interactions, valence-split sets of basis orbitals are used. The most recommended basis for describing interactions in multielectron systems is 6-31g basis or extended 6-31-$g(d)$ basis containing d-type atomic orbitals to take into account the polarization of the electron density of heavy metals.

For metals with even larger number of electrons, the lanl2dz valence-split basis set with effective core potentials (ECP) is recommended [34].

The energies in the condensed state were calculated [35−37] using the GAUSSIAN 03 software package [38]. The calculations were carried out at the temperature of 95 K and pressure of 10^5 Pa.

3. RESULTS AND DISCUSSION

Let us consider the process of electrocrystallization in a potentiostatic mode, in which an overvoltage on the substrate (η), namely, the self-diffusion of copper ad-atoms on a copper substrate is constant.

Figure 2 shows the values of the total energy (W) of copper crystal, which were calculated using formula (4) for different positions of diffusing nickel ad-atom during diffusion from position A into B.

The values of the activation energy of surface diffusion for adsorbed nickel and zinc atoms, which were calculated by formula (1), for various overvoltages of the substrate are given in Table 1.

The calculation results presented in Table 1 show that the value of the activation energy of surface diffusion depends on the potential of the surface (substrate in the case of electrocrystallization): with increasing potential, the activation energy value also increases. For example, for copper, as an increase in the overvoltage from 0.1 to 0.2 V, the E_S value increases from 0.19 to 0.26 eV for jump AB and from 1.76 to 2.11 eV for jump AC. Second, the activation energy value depends

on the jump length. With an increase in the jump length, in the case of the same number of nearest neighbors, the activation energy also increases. So, for the jumps AB and AC ($b_{AC} = \sqrt{2}b_{AB}$) E_S values are as follows: for copper at potentials 0.2 V, 0.1 V and 0−0.26 eV and 2.107 eV, 0.19 eV and 1.76 eV, 0.16 eV, and 1.13 eV.

An increase in the activation energy of surface diffusion with increasing surface potential is primarily associated with an increase in the binding energy between the ad-atom and the substrate [39−41].

The calculations are presented for diffusion in a fcc structure along the (100) plane. A good correlation between the obtained values of activation energies and the results of other researchers was found [3, 5, 42].
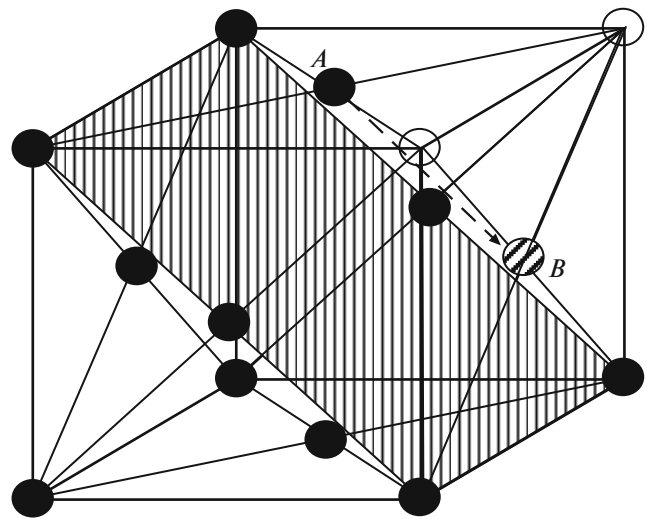

Fig. 3. Schematic of diffusion of ad-atom over the surface of fcc crystal in (110) plane: A is the initial position, B is the final position.
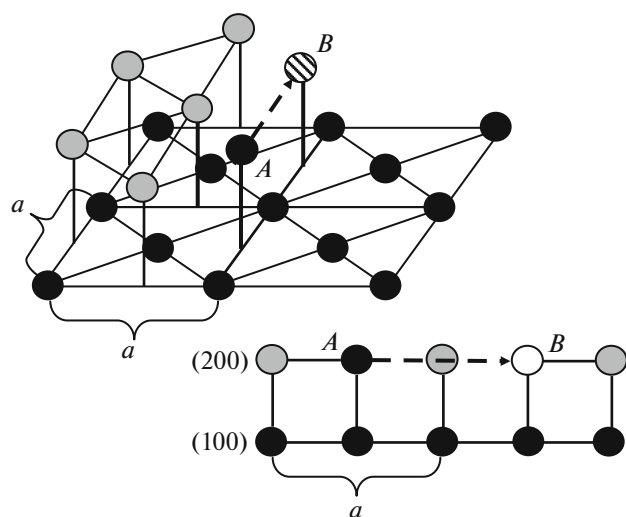
Fig. 4. Schematic of diffusion of ad-atom over the surface of fcc crystal ((100) plane and (200) growth step): A is the initial position, B is the final position.
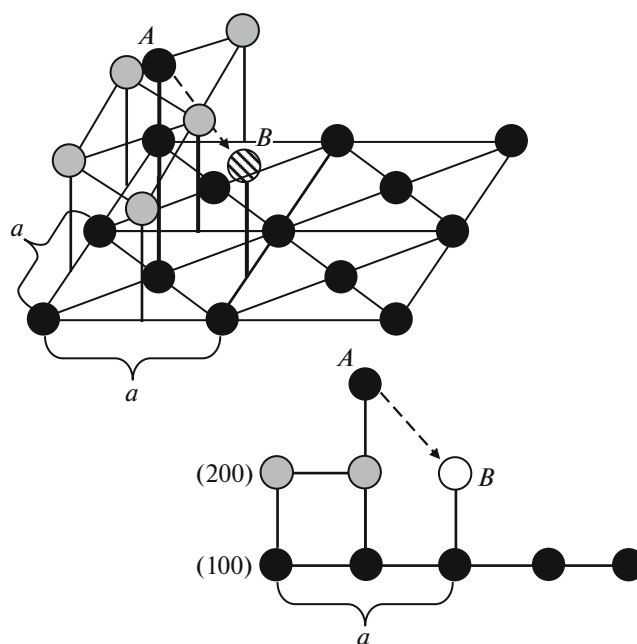

Fig. 5. Schematic of diffusion of ad-atom over the surface of fcc crystal above (200) growth step: A is the initial position, B is the final position.

Table 2 collects the values of E_S for self-diffusion of ad-atoms of copper ($\eta = 0.2$ V), nickel ($\eta = 0.5$ V), zinc ($\eta = 0.4$ V), and iron ($\eta = 0.3$ V) on a copper substrate along the (110) plane (Fig. 3).

Let us consider the case when diffusion occurs near the growth step. The gray atoms shown in Fig. 4 form a growth step and are in the plane (200). The self-diffusion of ad-atom occurs along the growth step.

In case of such diffusion, there is practically no dependence between the activation energy and the substrate potential. For example, as the potential decreases from 0.2 V to zero, the activation energy changes from 1.56 to 1.5 eV. An increase in the activation energy is primarily associated with an increase in the number of nearest neighbors, which also affects an increase in the binding energy.

The calculations show that the self-diffusion of ad-atoms is hampered in the vicinity of irregularities of crystal surfaces in comparison with a smooth surface. Consequently, the ad-atom has the ability to diffuse over the smooth surface during electrocrystallization, while, near the growth step, the probability of its diffusion decreases markedly.

Consider diffusion whose diagram is shown in Fig. 5. In this case, the ad-atom is above the atomic inhomogeneity in the form of a growth step and diffuses over the surface, occupying a more stable position in the (200) plane, thereby continuing the growth.

Figure 6 shows the values of the total energy (W_{total}) of copper crystal for different positions of the diffusing copper ad-atom during diffusion from position A (the diffusing ad-atom is above the growth step) into B.

It follows that the energy values in the initial (A) and final (B) positions are not equal for such diffusion in contrast to all the previous cases in which the ad-atom after diffusion over the surface occupied an equivalent new position. In this case, the ad-atom tends to occupy a position corresponding to the lowest energy of the crystal as a whole and the highest binding energy of the ad-atom. If the binding energy of ad-atom exceeds the value of its binding energy in position A, such diffusion is possible and occurs without overcoming the potential barrier. However, in this case, the obtained values of the energy of the crystal with ad-atom in the initial and final positions can be

Table 1. Activation energies of surface diffusion for different overvoltages on the substrate and different directions of jumping

Magnitude		Cu			Ni		Zn		Fe	
η, V		0.2	0.1	0	0.5	0	0.4	0	0.3	0
E_S, eV	AB	0.26	0.19	0.16	0.53	0.24	0.29	0.15	0.35	0.18
	AC	2.11	1.76	1.13	2.3	1.9	2.3	1.3	2.2	1.3

Table 2. Activation energies of surface diffusion of ad-atoms of copper ($\eta = 0.2$ V), nickel ($\eta = 0.5$ V), zinc ($\eta = 0.4$ V), and iron ($\eta = 0.3$ V) on the substrate along the (110) plane

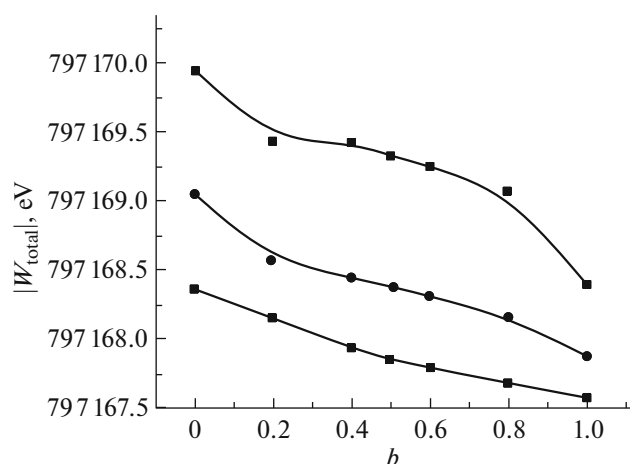| Magnitude	Cu	Ni	Zn	Fe
η, V	0.2	0.5	0.4	0.3
E_S, eV	0.39	0.77	0.42	0.55

Fig. 6. The values of total energy (W_{total}) for copper crystal as a function of length of jump (*b*) of ad-atom diffusing above the growth step from position *A* into *B*.

considered as the values of the activation energy of surface diffusion from position *B* into position *A*.

4. CONCLUSIONS

The proposed quantum mechanical approach makes it possible to calculate the activation energy of surface diffusion for various absorbed atoms. Contrary to other theoretical methods, in particular, cohesive approximation, this method accounts for the surface potential that is especially important in case of electrocrystallization on a substrate. The calculated E_S values are shown to strongly depend on the potential and on the surface geometry. The data obtained are in good agreement with the results of other researchers.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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