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## DEPOSITION OF Ni ATOMS ON THE IONIC (NaCl) AND METALLIC (Fe) SUBSTRATES

The deposition of a nickel on the foreign substrates is investigated by means of molecular dynamic simulation with pair potentials of different kinds independently of type of atomic interaction. An effect of energy of deposited atoms and surface defects on nucleation and growth of nickel islands is considered. The general trends can be explained in terms of the lifetimes and diffusion mobility of adsorbed atoms, the interaction between them and atoms of the substrate. The parts of deposited atoms in dependence on their kinetic energy as well as an amount of deposited atoms, which are needed to form a continuous film, are determined. Almost all Ni atoms with smaller energy (10000 K) join to the surface of the Fe-substrate. The obtained results confirm the theoretical point of view on the different deposition mechanisms in the cases of different substrates: the island (Folmer-Veber) mechanism in the case of Na-Cl substrate (mixture of haloid) and the layer-by-layer (Franc and Van der Merve) one in the case of metallic substrate.

**Keywords:** metal deposition, molecular dynamics simulations, surface diffusion, nucleation, fine-dispersed structure.

Вивчено осадження нікелю на підкладку методом молекулярно-динамічного моделювання з парними потенціалами різних видів залежно від типу атомної взаємодії. Розглянутий вплив енергії осаджених атомів і поверхневих дефектів на утворення і зростання островкових зародків нікелю. Загальні тенденції можуть бути пояснені тривалістю життя, дифузійною рухливістю адсорбованих атомів і взаємодією між ними і атомами підкладки. Ми знайшли частку осаджених атомів в залежності від їх кінетичної енергії, а також кількість осаджених атомів, при якій формується безперервна плівка. Майже всі атоми нікелю з більш маленькою енергією (10000 К) присоединяються до поверхні Fe- підкладки. Отримані результати підтверджують теоретичну точку зору про різні механізми осадження у випадках різних підкладок: островковий механізм (Фольмера - Вебера) у разі підкладки Na-Cl (суміш галоїду) і пошаровий механізм (Франка і Ван дер Мерве) у разі металевої підкладки.

**Ключові слова:** напилення металу, молекулярно-динамічне моделювання, поверхнева дифузія, зародження, тонкодисперсна структура.

Изучено осаждение никеля на подложку методом молекулярно-динамического моделирования с парными потенциалами различных видов в зависимости от типа атомного взаимодействия. Рассмотрено влияние энергии осаждающихся атомов и поверхностных дефектов на образование и рост островковых зародышей никеля. Общие тенденции могут быть объяснены продолжительностью жизни, диффузионной подвижностью адсорбированных атомов и взаимодействием между ними и атомами подложки. Рассчитаны доли осажденных атомов в зависимости от их кинетической энергии, а также количество осажденных атомов, при котором формируется непрерывная пленка. Почти все атомы никеля с более маленькой энергией (10000 К) присоединяются к поверхности Fe- подложки. Полученные результаты подтверждают теоретическую точку зрения на различные механизмы осаждения в случаях различных подложек: островковый (Фольмера - Вебера) в случае подложки Na-Cl (смесь галоида) и послойный (Франка и Ван дер Мерве) в случае металлической подложки.

**Ключевые слова:** напыление металла, молекулярно-динамическое моделирование, поверхностная диффузия, зарождение, тонкодисперсная структура.

## 1. Introduction

It is known that the condensed films can be either continuous, starting already from a monoatomic layer, or to consist of the separate isolated particles (islands). And it renders large influence on subsequent structure and properties of the condensed films.

Mathematical simulation of the atom deposition is indispensable to understand the stages of film formation, the arising, and the growth of nucleus. Their structure caused by these processes is practically inaccessible for experimental researches.

There are many unresolved questions, concerning the deposition of the high energy atoms by plasma-ionic scattering. Such experiments are widely applied to obtained new structure and phase states of alloys. At least, fine-dispersed structures were obtained in many works, for instance in Ref. [1-5].

The most known works, concerning the deposition from the gas phase, are fulfilled by means of Monte Carlo simulations, for instance [6-10]. The bond-counting kinetic Monte Carlo (KMC) method is widely used. The key point in this technique is the calculation of activation energy for the surface atom diffusion. In order to calculate the activation energy, the contribution of the surrounding atoms in the initial position or of the difference between the number of the nearest atoms in the initial and the final positions are only taken into account in most of the proposed models (see in Ref. [10]). The atom states during diffusion jumps are not considered. Thus, the simulation with using KMC method has an essential limitation concerning their correspondence to reality.

Many papers with modeling of atoms deposition by the molecular dynamics (MD) method appeared in the recent years, for instance [11-16]. The main problem of such method is the values of the time step (of order 1–2 fs) which are usually applied in the simulation. It is not enough small to reach needed accuracy of calculations as the deposited atoms penetrates in areas of large repulsion forces. Therefore, in many papers, simulation of clusters placed on the surfaces or falling onto them are considered. At the small time steps, only unrealistically high energy atom, which flows to the surfaces, can be considered. Thus, the new works on the modeling of deposition process are necessary for the correct study and visualization of mechanisms of thin film formation. A focus of interest in our work is the formation of centers of condensation.

The very porous Ni-films were obtained as results of simulation in the case of the Si substrate [15]. We use other substrates and much smaller timestep (0.2 fs) for correct investigation of the condensation mechanisms.

## 2. Details of the simulation

The MD simulation was fulfilled using our program for parallel computing. The interactions between the metal atoms were described by potentials of the embedded atom type, elaborated in work of Bonny [17]. We included into impute file the tables of EAM potentials from repository (see <http://www.ctcms.nist.gov/potentials/>) in 5000 point each. Interaction between pairs of atoms Na-Na, Na-Cl and Cl-Cl was calculated using the Born–Mayer–Huggins potential specified by Fumi and Tosi in paper [18]. Such potentials were slightly modified to insure the right melting temperature (with accuracy in 10 K) after decrease of the cut-off radius up to 0.8 nm. For Ni-Na and Ni-Cl pairs the used potentials were nearly the same ones as for Na-Cl with the reduced minimal energy ( $\epsilon_{\min} = -0.29$  eV,  $d_{\min} = 0.295$  nm for Ni-Na, and  $\epsilon_{\min} = -0.29$  eV,  $d_{\min} = 0.325$  nm for Ni-Cl pair). Certain prefactors were used in the program to change the values of energies and forces for these pairs. Parallel calculations were fulfilled by means of Graph processors (NVIDIA graphics-cards) with the help of CUDA software.

All simulations employed the Verlet algorithm with a time step of 0.2 fs in the case of the NaCl-substrate and 0.5 fs in the case of Fe-substrate. The weak thermostating for the substrates was chosen in all cases; in our program, a multiplier to velocity of atoms was  $1 \pm 0.001\sqrt{(|T-T_t|/T)}$  ( $T$  is an instantaneous temperature,  $T_t$  is the set temperature, sign “+” if  $T < T_t$ ).

The first step before simulations was preparing of samples for simulations. The total number of atoms was 16384. Only the bottom layer of the substrate contained atoms with stationary positions, which correspond to structure of substrate materials (Na-Cl or Fe). In upper 6-10 layers, atoms of the substrate were placed initially in right positions, and their movement was simulated; thermostating was applied for them. All atoms of the deposited element (Ni) were placed randomly in one plane above the substrate; their interaction was not considered. Periodically, one of deposited atoms began movement in the direction to the substrate (only 1/3 part of its kinetic energy was related to the movements in the directions parallel to the substrate). Atoms, which were reflected from the substrate or torn out atoms of the substrate, were removed into the plane placed above the plane with atoms for depositions.

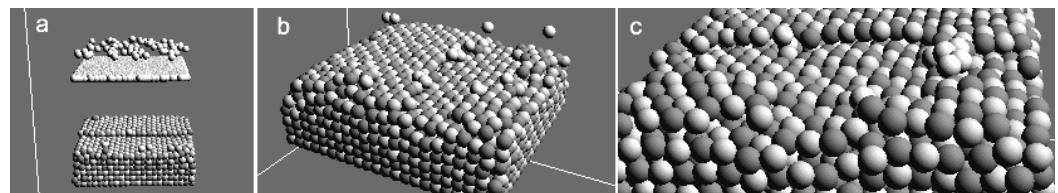
A process of deposition was continuously imaged on the screen of monitor. And one can change the angle of viewing and to make an enlargement of current images.

For analyzing the results of simulations, we use the program, which enables viewing with the step in one angstrom all sections of the model with coordinates of atoms from saved files (the brightness of images of atoms placed behind of chosen section depended on their distance from the section). Thus, centers of crystallization, which arises in deposited liquid drops, could be determined visually; their structure was verified studying graphs of the local radial pair distribution functions (LRPDF) – they were calculated by the same program. Knowing the location of the crystallization centers, we studied changes in structure of these areas in the past, using the results of the earlier saved files, so we can define the time of appearance of the crystallization center within a few picoseconds. In the mentioned program, all the volume in consideration was marked out with cube cells (an edge  $l = 0.5$  or  $0.7$  nm). When moving a cursor to the image of atom (for the section in which it was brightest), the values of his number and coordinates of small cell were writing in the message windows. It allowed studying the environment of concrete atoms or determining the LRPDF.

### 3. Results and their discussion

As it was mentioned above, only high flows of atoms may be considered at nowadays; we considered the flows from 500 to 3000 atoms/( $a^2 \cdot s$ ) for the NaCl substrate (is the area per one atom site). In the case of this substrate a collision at falling of deposited atom is almost elastic and the greater part of atoms is reflected from the surface. The falling atoms accelerated at approaching to the surface of the substrate by attractive forces. Therefore, those atoms, which become adsorbed atoms, have sufficiently large velocities of moving at the surface and their lifetime in adsorbed state is not large. Trajectories of movement of adsorbed atoms are intricate; their distant from the averaged surface plane changes all time.

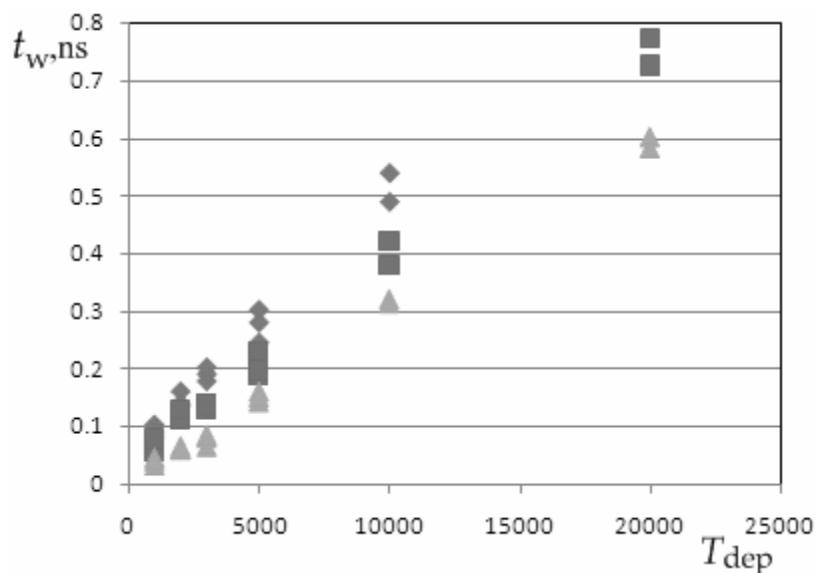
At flows less than 1000 atoms/( $a^2 \cdot s$ ), we usually see only one adatom, seldom two atoms. To increase the average lifetime of adatoms we input the crystal step in initial conditions for the substrate (Fig. 1). Thus, we could to determine the waiting time for appearing of nucleus of condensation. After that, the ratio of deposited and evaporated atoms began increasing. And it was possible to determine the dependences of the waiting time on the energy (temperature) of deposited atoms and intensity of their flow.



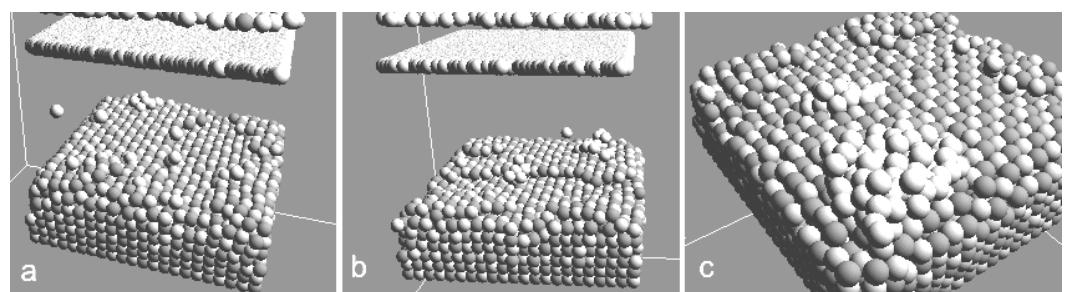
**Fig. 1. Deposition of Ni-atoms on the NaCl-substrate,  $T_{dep} = 5000$  K;  $T_{substr} = 300$  K;  $I = 1721$  atoms/ $(a^2 \cdot s)$ , the time of deposition  $t = 40, 128$  and  $168$  ps; Ni-atoms are lightest.**

Nuclei of deposition from less than 4 atoms broke up often. Fig. 2 shows the waiting times of appearance of such group from 4 atoms which becomes in feature the growing deposited center.

Fig. 3 shows growth of the centre of condensation. A majority of adsorbed atoms joins to the centers when those become sufficiently big. The comparatively big drop in Fig. 3, c is liquid, as it is frequently distorted by irregular oscillation of the substrate surface in result of blows by falling atoms.

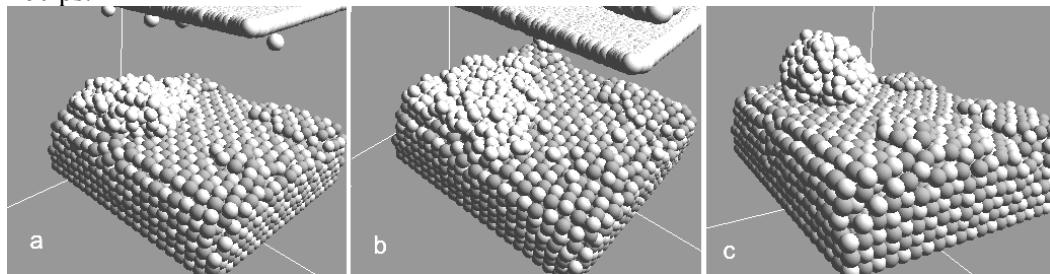


**Fig. 2. The waiting times for appearance the first group from 4 deposited atoms, – flow  $I = 860$  atoms/ $(a^2 \cdot s)$ ; ■ –  $I = 1720$  atoms/ $(a^2 \cdot s)$ ; ▲ –  $I = 2580$  atoms/ $(a^2 \cdot s)$ .**



**Fig. 3. Growth of the centers of condensation,  $T_{dep} = 5000$  K,  $I = 1720$  atoms/ $(a^2 \cdot s)$ ; for a,b,c time  $t = 0.295, 0.530$  and  $0.820$  ns, Ni-atoms are lightest.**

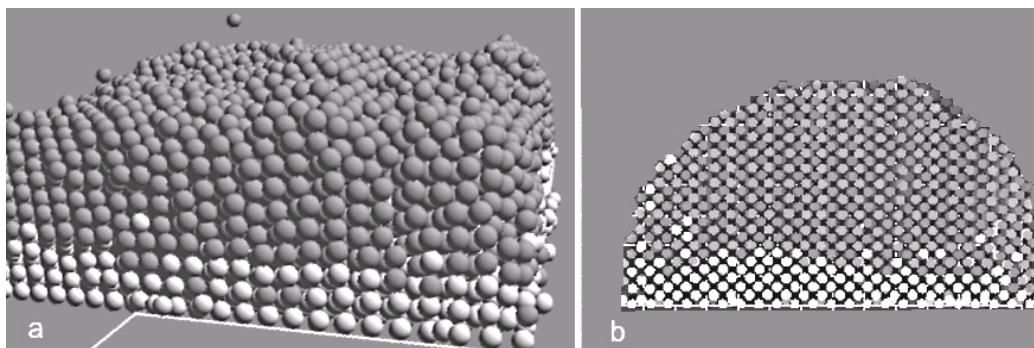
To determine at which size of the drop the crystal nuclei arise in it, it is necessary to exclude the flow or set it very small in accordance with the experimental conditions. In this way, we studied sufficiently large drops. And we change the interaction of Ni-atoms with atoms Na and Cl (increasing and decreasing it in 2 times) to study an equilibrium form of the condensation centers at different energies of adsorption. Examination of sections of the drops shown in Fig. 4, a-c gives evidence of forming of crystallization center in their central part. The waiting time of crystal nucleus forming depends on the drop shape. The crystal nucleus is formed in drop of 360 atom (it is shown in Fig. 4, c) less than 170 ps after stopping of deposition. Whereas in large drop of 670 atoms, which is like that is shown in Fig. 4, b, the waiting time for crystal nucleus appearing is roughly 260 ps.



**Fig. 4. Forms of the center of condensation at different interactions of Ni atoms with the substrate,**

$T_{dep} = 5000 \text{ K}$ ,  $I = 1720 \text{ atoms}/(a^2 \cdot \text{s})$ ; for a,b,c time  $t = 2.295 \text{ ns}$ ,  
 $800 \text{ ns}$  at small flow ( $I = 17.2 \text{ atoms}/(\text{m}^2 \cdot \text{s})$ ); Ni-atoms are light.

Thus, the Folmer–Veber islet mechanism is takes place in the case of Ni deposition on the NaCl substrate that coincides with experimental works for many metals on halides.



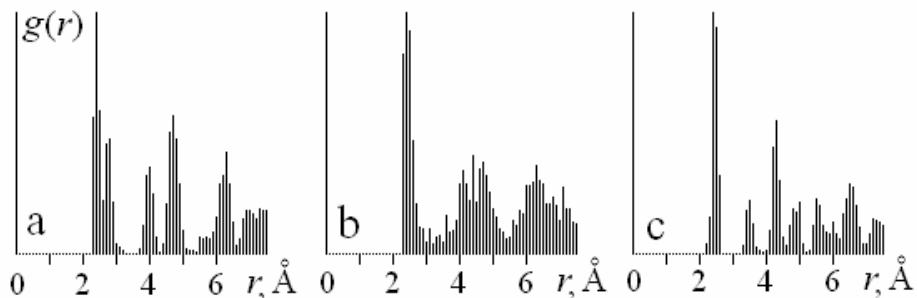
**Fig. 5. Deposited films of Ni on the Fe-substrate,**  
 $I = 1720 \text{ atoms}/(a^2 \cdot \text{s})$ ;  $t = 18000 \text{ ps}$ ; a –  $T_{dep} = 10000 \text{ K}$ , b – a section of the film,  $T_{dep} = 150000 \text{ K}$   
Fe-atoms are light.

Absolutely another way of condensation takes place in the case of deposition Ni-atoms on the Fe-substrate. Fig. 5 shows the films from deposited Ni-atoms with different kinetic energy. Here the majority of Ni-atoms occupies stationary site at once or after brief diffusion on the surface. The majority of falling atoms with joins to the Fe-substrate. At high kinetic energy (Fig. 6, b, the temperature 150000 K is equivalent to the energy ~13 eV) roughly 6% from the all quantity of falling atoms reject from the surface and there are also events when Fe-atom are beaten out from the substrate (the ratio of falling and beaten out atoms is 0,1 on average from the beginning). After a full layer of Ni is formed, the part of rejected atoms becomes smaller. Atoms with energy 10000 K reject

rarely from the surface even at the beginning. Fig. 5,a shows the section of the Ni-film at deposition of not high energetic atoms (10000 K). As one can see, an outward upper surface of the film is wavy; the difference in height is 1-3 layers.

From the beginning, the structure of deposited Ni remains bcc; after deposition of 5-6 layers the fcc atomic structure appears. However, we did not see forming nuclei of the fcc phase.

The structure changes gradually. Even in comparatively thick film, the structure of sections outwardly resembles the distorted bcc structure. However, local  $g(r)$  – RPDFs, unambiguously corresponds to the fcc structure. Fig. 6 shows 3 RPDFs obtained within spheres with a radius of 7.5 nm for 15 central atoms placed in the 3-rd, 7-th and 16-th layers from the bottom in the cases a, b, c. The first of them (Fig. 6,a) corresponds to the bcc structure; while the second LRPDF (Fig. 6,b) is intermediate between those that correspond to the bcc (Fig. 6, a) and fcc (Fig. 6, c) structures.



**Fig. 6. Local radial pair distribution function obtained from different layers of Ni-films on the Fe-substrate,  $I = 1720 \text{ atoms}/(\text{a}^2\cdot\text{s})$ ;  $t = 18000 \text{ ps}$ ;  
a –  $T_{\text{dep}} = 10000 \text{ K}$ , for a,b,c n = 3, 7, and 16 (the number of layers).**

In the case of the high energy (150000 K) of falling atoms, ~6% from them is reflected from the metal surface. Almost all Ni atoms with smaller energy (10000 K) join to the surface of the Fe-substrate. Continuous film of Ni is formed after deposition of that number of atoms which responds to 3.3 full layers. In thick films the surface is wavy with the thickness in 2-3 layers.

#### 4. Conclusions

It is shown that some part (of about 6%) of the falling high energy (150000 K) atoms is reflected from the metal surface. Almost all Ni atoms with smaller energy (10000 K) couple with the surface of the Fe-substrate. The number of Ni atoms, which is needed to form continuous film after deposition, is found to be correspondent to 3.3 full layers. Thus, our results confirm theoretical viewpoints on different mechanisms of deposition in cases of different substrates: the islet (Folmer-Veber) in the case of Na-Cl substrate (the haloid compound) and layer-by-layer (Franc and van der Merve) in the case of the metallic substrate. However, direct simulation gives an additional information on details of these processes and more full information about the structure of the first layers.

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