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Modeling of growth process on the surface of crystals

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The article is devoted to modelling the growth of thin films on the surfaces of crystals having a similar crystal structure with a small parameter of mismatch of the lattice of substances from which the film and the crystal substrate are formed. A review of modelling methods based on both analytical expressions and computational methods is made. A number of methods for modelling the most typical processes: surface formation in the form of pyramidal formations (so-called needle crystals), two-dimensional with initial islands of growth and three-dimensional uneven growth processes. To model the process of growth of needle crystals, it is proposed to use a method based on Gaussian statistics of surface height increments. The model of three-dimensional growth of the crystal surface, which uses the iterative algorithm of Foss, and which makes it possible to investigate the processes of stepped, uneven growth of crystals, is also considered. In contrast to stepwise growth, a model of submonolayer growth of a film based on the Monte Carlo method is considered. For submonolayer growth of the film, pseudo-random sequences are used, which simulate the initial arrangement of the nuclei of the nucleus of the next layer on the crystal surface. The computational characteristics of this method are determined, namely the dependence of the number of iterations on the initial surface filling coefficient

Keywords: Monte Carlo method, crystal growth, analytical methods.

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Introduction

The development of mathematical models describing the growth of thin films and needle-like crystals on smooth, pre-treated surfaces began in the middle of the last century. The efforts of many researchers have focused both on finding analytical solutions and on improving the efficiency of complex computational methods. The basis of analytical methods are such sections of mathematics as the theory of deterministic point processes and the theory of stochastic matrices [1]. The combination of all the above methods forms the lattice theory, which is one of the modern scientific areas of mathematical and statistical physics [2]. A number of problems for which precise analytical solutions have been found can confirm the performance of this approach: the six-vertex model [3] and deterministic point processes [4]. Classification of problems and methods of their solution, which are the subject of modern statistical mechanics, is shown in Fig.1.

The most common algorithms that have become the basis of computational methods are the Monte Carlo method and molecular dynamics [5, 6].

One of the most common divisions of methods for modelling film growth processes is the division into discrete and continuous methods. The method of molecular dynamics is a continuous method. This means that the substances involved in the growth of the film are considered as some mass distributed in volume. This method is convenient when one of the substances is in a liquid (solution or melt) state [7].

In addition to the well-known Monte Carlo method, discrete methods for modelling surface growth include methods for constructing fractal surfaces, one of which is the Foss method [8], which we use.

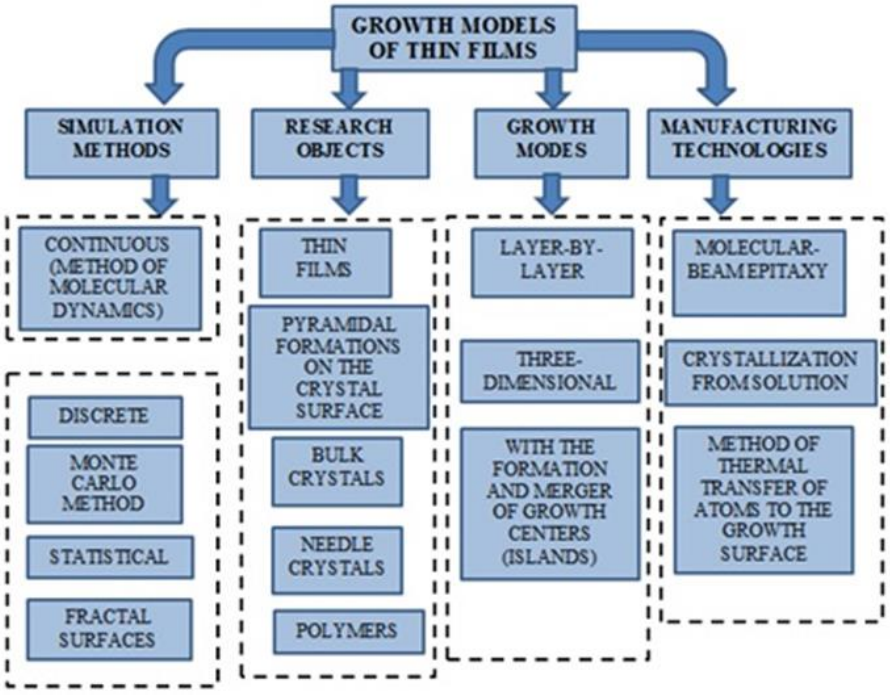

Fig.1. Problems of modelling the growth of thin films and methods of their solution.

Theoretical and experimental studies of surface growth patterns show that the growth process is self-similar in both temporal and spatial scales. That is, the increase in surface area and its height are coordinated by a certain scale ratio. It turns out that there are several numerical relationships between the growth rates of the surface along and in the perpendicular directions, they characterize some specific growth regimes, they are called universal classes.

The most well-known statistical models of growth include such as deterministic point process and six-vertex model. Modern and most generalized theoretical ideas about the growth of crystalline and/or polymer structures use the concept of renormalization group [9]. The renormalization group provides the most common means of studying a significant group of phenomena in physics and chemistry, such as crystal growth processes, and in particular the growth of thin films on the crystal surface.

I. Main part

One-dimensional models based on the analytical expression of the dependence of the height of the "needle" on time can be used to model the growth of needle-like crystals. These models can continue and complement the known models of growth of needle-like crystals. One of them is a model based on the Gibbs-Thomson effect, which allows to correctly determine the growth rate of the crystal and its critical diameter [10].

Modelling of submonolayer growth, which can be considered two-dimensional, was carried out based on the Monte Carlo method. The initial condition of the method is a given distribution of growth centres on the

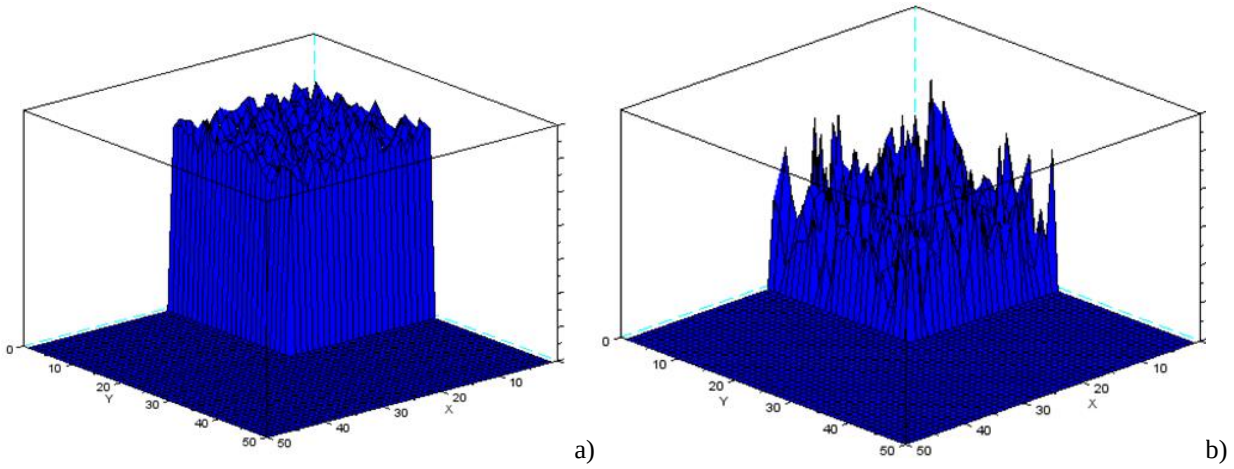

Fig.2. One-dimensional growth modes for different values of model parameters: (a) $c_1 = 0.1$, $c_2 = 8$, mξ = 0.1, $\sigma_\xi = 0.01$; (b) $c_1 = 0.1$, $c_2 = 16$, $m_\xi = 0.1$, $\sigma_\xi = 0.08$.

surface of the crystal, followed by determining the number of occupied nodes of the lattice, closest to the given. We have constructed the growth surfaces of the submonolayer for different degrees of filling the growth surface with the initial growth islands. The main result of the research is the dependence of the surface filling rate on the number of initial growth islands.

Modelling of the three-dimensional surface growth process is performed by the Foss method, which is based on the iterative addition of statistically independent increments for each point of the two-dimensional surface that simulates the initial surface of the crystal.

II. One-dimensional growth model based on deterministic point process (needle surface growth modelling)

The least complex model of three-dimensional growth of the film surface is a model in which the atoms that reach the crystal surface "stick" to it and do not move further. Statistical features of the growth process depend on the technological parameters of the process: the rate of atoms and the distribution of this characteristic depending on the coordinates of the crystal surface, but the general dependence of film height on time [11] is determined by expression (1)

$$h(t) = c_1^{-1} \cdot t + \xi \cdot c_2 \cdot c_1^{-\frac{3}{2}} \cdot t^{\frac{1}{2}}, \qquad (1)$$

where c_1 and c_2 are numeric constants, ξ is a random variable with a Gaussian distribution.

Therefore, the growth process described by expression (1) has 4 parameters: coefficients c_1 and c_2 and the mathematical expectation m_ξ and the variance σ_ξ of the random variable ξ.

The three-dimensional surface modelled by relation (1) is shown in Fig.2. As can be seen from the shape of the formed surface, this model makes it possible to describe the growth of needle-like crystals or other formations on the surface, the cross section of which is negligibly small compared to the height. This regime occurs when the energies of the atoms trapped by the upper layers are insufficient to transition to adjacent layers of the crystal structure, and therefore the filling of the lower atomic layers (i.e., the transition to two-dimensional mode of crystal film growth) does not occur. Comparing the images in Fig. 2, we see that by appropriate selection of the values of the model parameters it is possible to model both the growth of the surface with pyramid-like formations with a small almost identical height (Fig. 2a) and the growth of more complex formations (Fig. 2b).

The formation of structures with needle-like crystals having a characteristic cross-sectional size of the order of nm2 are widely used in modern science-intensive technologies. Crystals with needle-shaped or pyramidal formations on the surface of the same material as the substrate material have a low reflection coefficient in a wide range of solar radiation, which makes them attractive in terms of use in the production of solar cells [12], photonic crystals [13] and biosensors [14, 15]. Such films can be used in a wide range of temperatures for the production of sensor elements based on nanosized poly-silicon films [16], local 3-dimensional integrated silicon-insulator structures [17], as such films can be resistant to destruction if applied protective coating.

III. Modelling of the mechanism of three-dimensional (non-uniform) surface growth

The most complex and least studied growth process is stepwise, uneven crystal growth, as only three-dimensional growth models can be applied to it. The three-dimensional mechanism is becoming increasingly important in the development of nanotechnology, as it is possible to control the position of each individual atom with an accuracy of several nanometers.

Consider the method of fractal surface formation based on the iterative Foss algorithm [8]. Foss's algorithm forms a fractal relief gradually, shredding the elementary cells of the grid at each step of the algorithm. As is known from theory, fractals are divided into levels. In the Foss algorithm, the surface of each subsequent level contains all points on the surface of the previous level and some new set of points. In this case, every four points on the surface of the previous level form an additional five points of the next level: four points in the middle of the sides that form the cell of the previous level and one point at the intersection of diagonals, as shown in Figure 3.

Each point of the lattice on the initial plane corresponds to one point of the fractal surface, which is formed in the next step of the iteration. At the beginning of the algorithm, each of the four points of the initial lattice defines one point of the fractal surface, and the value of the height is assigned some random number from the sequence having a Gaussian distribution. The height of the points of the fractal surface of the next level

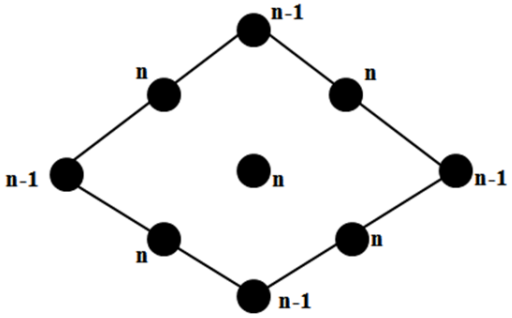

Fig.3. Scheme of formation of fractal points (one cell), n means the fractal level number to which the formed points belong.

is defined as the average value of the heights of the points of the previous level, which are on the same edge with this point. For the point in the center of the cell, the height is defined as the average height of all four points of the previous level. Then some random number from a series of random numbers with Gaussian distribution is added to the found values, the variance of this series is

related to the variance of the series used at the previous level, relation (2):

$$\sigma_n^2 = (1/2)^{2\cdot H} \cdot \sigma_{n-1}^2, \qquad (2)$$

where H is the Herst index, or the self-similarity parameter of the formed fractal series, n is the iteration number,σ_n^2 та σ_{n-1}^2 – squares of variances in successive iteration steps.

Figure 4 shows an example of a fractal surface constructed according to the Foss algorithm in the fourth step of the iteration with the Herst index $H = 0.1$ and the initial variance$\sigma_1^2 = 0.1$.

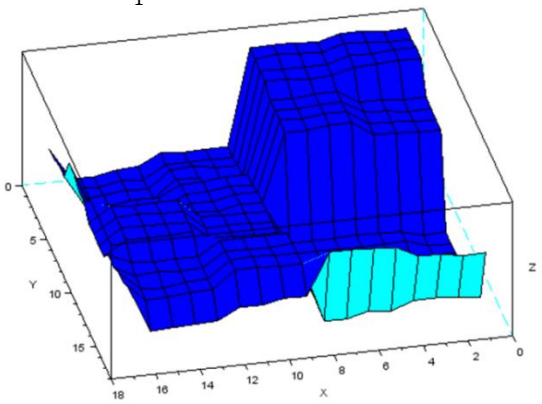

Fig.4. The fractal surface is constructed on the fourth step of iteration of the Foss algorithm with Herst index H=0.1 and initial dispersion σ_1^2=0.1.

The self-similarity of the Foss method makes sense in that there is some correspondence between the variances of random fluctuations in the height of the nodal points at each step of the algorithm (expression 2). This can be concluded from the graphs of growth of the standard deviation of the height of the surface constructed for different Herst indicators, which are shown in Fig.5.

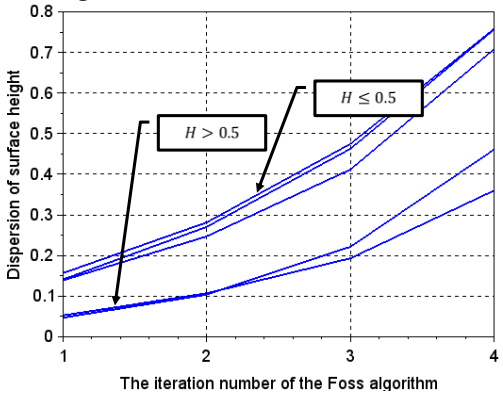

Fig.5. Graphs of growth of surface height variance for different Herst indices.

The graphs show that the surface growth process differs significantly for two different sets of Hurst values: $H \leq 0.5$ and $H > 0.5$, and for the second set of Herst values the surface growth is less intense. Within one group of Herst indicators, growth processes are almost slightly different from each other, and the slight difference in standard deviation can be explained by different statistical samples for surface growth processes.

IV. Modelling of two-dimensional growth

Modelling the growth processes of submonolayer films is an important task, and its solution can significantly improve the technological processes of film growth in semiconductor production. The most common method of modelling the growth of submonolayer films is the Monte Carlo method, which is based on the probability of filling the atom of the sprayed substance of the free node [18]:

$$P_i \sim \exp\left(-\frac{E_{A(i)}}{k_B T}\right), \qquad (3)$$

where P_ii is the probability of filling the free node of the submonolayer i; $E_{A(i)}$ is the activation energy of the process; k_B is the Boltzmann constant; T is the substrate temperature.

We have developed and implemented an algorithm that simulates the mechanism of two-dimensional submonolayer growth of a crystal film of simple cubic structure using an island mechanism, where the criterion for filling the node is the number of nearest filled nodes. The initial condition for the algorithm is the presence of growth islands with filled nodes of the submonolayer of the film. Such growth islands can be formed at the stage of the previous cycle of surface treatment by introducing substances that are catalysts of the growth process, or surface treatment by ion implantation.

At the beginning of the algorithm on a matrix of size 50×50, which simulates the surface on which the film grows, we randomly set the growth islands. The relative share of islands in the total number of matrix elements is an additional modeling parameter. In fig. Figure 6 shows the state of the surface with relative proportions of growth islands: 12%, 18% and 25%, which are randomly placed on the crystal surface.

The number of filled nodes that are closest to the specified determines the condition of filling the film layer in some node. If the number of filled nodes exceeds or is equal to half of all closest to this, the upper layer is formed. For angular elements of the matrix, this means that the top layer must be formed in more than one node, for boundary nodes along the face of the crystal - more than two, and in nodes that are not on the edge of the crystal surface - more than four.

In fig. 7 shows the filling of the crystal surface at different stages of film growth: 33%, 66% and almost 100% of the filling of the surface for the initial value of the filling factor of the surface which is 12%.

For a surface with an initial filling of 12%, these phases correspond to the 18th, 41st and 77th iterations of the algorithm.

In our model, the rate of film formation obviously depends on the initial coefficient of filling the surface with growth islands. The graph of this dependence is shown in Fig.8.

Analysis of the developed algorithm shows that reducing the proportion of initial filling leads to the fact that the surface no longer has nodes that meet the conditions for the formation of a new layer, although much of the surface remains uncovered by the new layer.

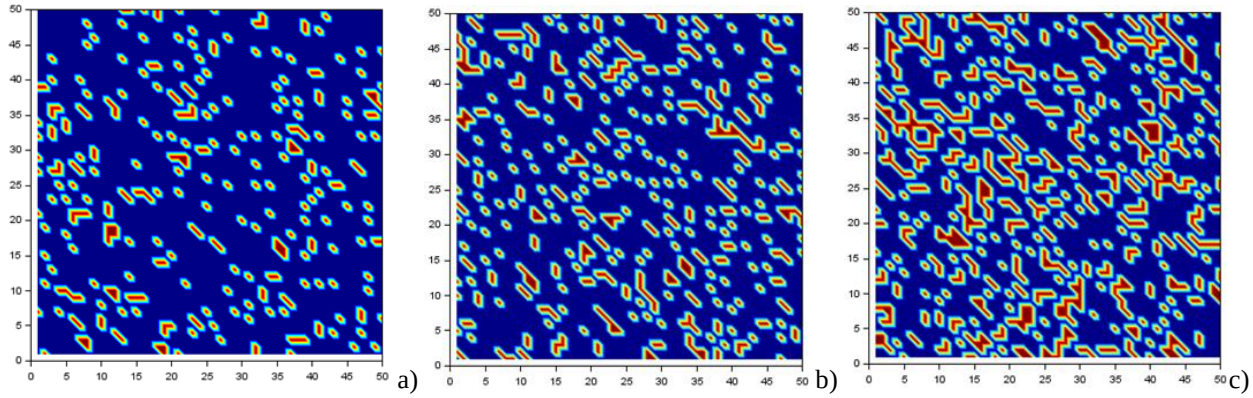

Fig.6. Initial film formation of growth islands on the crystal surface (11%, 18% 25% in fig. a, b and c, respectively).

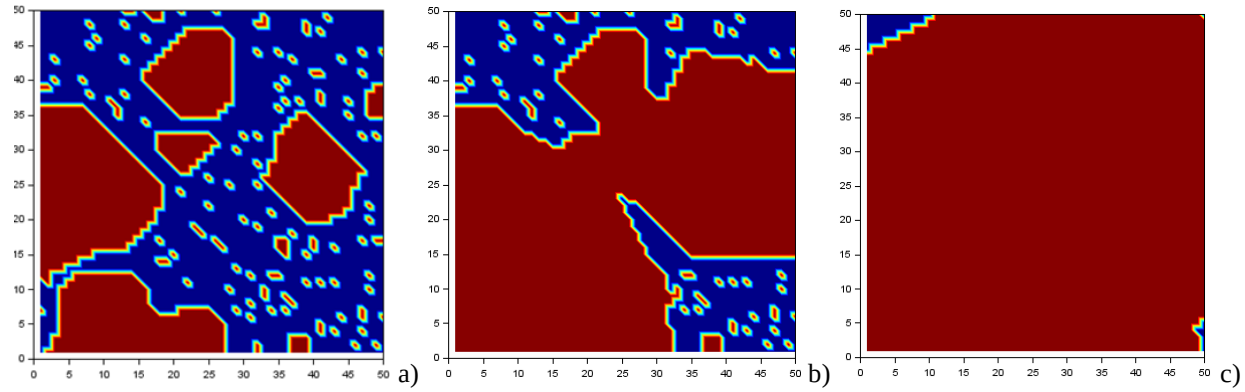

Fig.7. Initial formation of growth islands on the crystal surface (12%, 18% 25% in Fig. A, b and c, respectively).

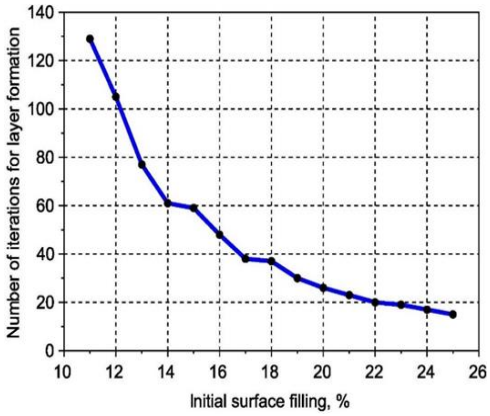

Fig.8. Graph of the dependence of the number of cycles required to build a single layer from the initial filling factor of the growth surface.

In fact, the growth of the next layer will begin, i.e. there may be a transition to a three-dimensional process of film growth, which may be an undesirable effect. That is, at low fill coefficients of the initial growth surface, there are configurations of the initial islands, at which high-quality two-dimensional film growth is observed. Identifying all possible initial configurations conducive to two-dimensional growth is a task that requires significant computing power. We present estimates of complexity for the parameters of the problem we used to model two-dimensional growth. The matrix defining the initial surface has a dimension of 50 × 50. The formation of a new layer does not occur if the fill factor is less than 10%, ie it is 250 knots of the initial surface. Thus, the number of different ways to place the islands of growth N is determined by formula (4):

$$N = C_{2500}^{250} = \frac{2500!}{250!\cdot 2250!} \approx \frac{2500^{2500}\cdot\sqrt{5000\cdot\pi}}{250^{250}\cdot 2250^{2250}\sqrt{500\cdot\pi}\cdot\sqrt{4500\cdot\pi}} = \frac{2500^{2500}}{250^{250}\cdot 2250^{2250}\cdot\sqrt{450\cdot\pi}} \quad (4)$$

or

$$ln(N) = 2500\cdot ln(2500) - 250\cdot ln(250) - 2250\cdot ln(2250) - ln\left(\sqrt{450\cdot\pi}\right) \approx 130, \text{ so, } N = e^{130}.$$

To initially fill the crystal surface with islands at the level of 11%, among 40 variants of random initial placement of islands, 36 island locations were identified, leading to complete filling of the surface with the second layer for 69, 77, 83, 88, 93, 98, 105, 110, 120, 130 and 145 iterations.

Obviously, the choice of the initial location of the islands is of scientific and practical importance. By conducting a numerical experiment, we determined several initial configurations for low coefficients of filling the crystal area with the growth centres of the second layer of the film.

Discussion of results and conclusions

We have considered the main mechanisms of formation of crystalline films on a flat surface: two-dimensional, three-dimensional and growth of needle crystals. The Foss algorithm is considered for the three-dimensional growth regime. One-dimensional statistics of crystal height increments, which obviously depends on two factors - the rate of adsorbed atoms and the rate of evaporation, can be used to model the growth of needle crystals, which is important for use in modern materials for nanoelectronics.

We have also proposed an algorithm for constructing a crystal surface that simulates the process of two-dimensional growth or film growth in the form of a submonolayer. For the algorithm to work, you need to specify the initial foci of new surface formation, which may be related to the technological features of the application of films in the form of catalysts for the crystallization process, such as local introduction of impurities or surface treatment. The most important characteristic of the algorithm is analysed - the initial coefficient of surface filling with growth islands, and the quantitative influence of this coefficient on the surface growth rate is determined, which is determined by the number of iterations required for transition from initial to fully formed submonolayer film. The number of nearby nodes in which the adsorbed atoms are deposited determined growth statistics during each iteration. The algorithm developed by us can potentially be used to model the processes of transition from two-dimensional to three-dimensional mechanisms of film growth on the crystal surface.

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[1] Tracy, Craig & Widom, Harold. On orthogonal and symplectic matrix ensembles. Communications in Mathematical Physics 177, 727 (1996); https://doi.org/10.1007/BF02099545.
[2] Tetsuo Deguchi, Introduction to solvable lattice models in statistical and mathematical physics, (2003); https://doi.org/10.1201/9781420034615.ch5.
[3] Andrea Levi, & Miroslav Kotrla Theory and Simulation of Crystal Growth. Journal of Physics Condensed Matter 9, 299 (1996); https://doi.org/10.1088/0953-8984/9/2/001.
[4] O. Kallenberg, Foundations of Modern Probability, Second Edition, Springer, 2002.
[5] Marcus Turowski, & Marco Jupé, & Henrik Ehlers, & Thomas Melzig, & Andreas Pflug, & Detlev Ristau, Simulation in thin film technology. Conference: Proc. SPIE, Optical Systems Design 2015: Advances in Optical Thin Films 9627 (2015); https://doi.org/10.1117/12.2191693.
[6] S.Piana, & J. Gale Three-dimensional kinetic Monte Carlo simulation of crystal growth from solution. Journal of Crystal Growth 294, 46 (2006); https://doi.org/10.1016/j.jcrysgro.2006.05.020.
[7] Asmae, Elalami, "Three-dimensional numerical simulation of crystal growth using TSM under g-jitter conditions" Theses and dissertations. Paper 776 (2008).
[8] R.F. Foss Fundamental Algorithms in Computer Graphics. Berlin: Springer Verlag, 805–835 (1985).
[9] Mark Bowick, & Alex Travesset The Statistical Mechanics of Membranes. Physics Reports 344 (2000); https://doi.org/10.1016/S0370-1573(00)00128-9.
[10] A.O. Druzhynin, et el. Analysis of growth kinetics of silicon nanoviskers, Nanosystems, nanomaterials, nanotechnologies 9(4), 933-940 (2011).
[11] Alexei Borodin, & Vadim Gorin Lectures on integrable probability, (2012).
[12] R.L. Politanskyi, M.V. Vistak, G.I Barylo and A.S. Andrushchak, Simulation of anti-reflecting dielectric films by the interference matrix method, Optical Materials 102, 109782 (2020).
[13] Brendan Kayes & Michael Filler & Morgan Putnam & Michael Kelzenberg & Nathan Lewis & Harry Atwater. Growth of vertically aligned Si wire arrays over large areas with Au and Cu catalysts. Applied Physics Letters 91 (2007) https://doi.org/10.1063/1.2779236.
[14] M. Vistak, Z. Mykytyuk, F. Vezyr, V. Polishchuk, Cholesteric-nematic mixture as a sensitive medium of optical sensor for amino acids. Molecular Crystals and Liquid Crystals 672(1), 67 (2018).
[15] O.Sushynskyi, M. Vistak, Z. Gotra, F. Andriy, Z. Mikityuk, Silicon dioxide nanoporous structure with liquid crystal for optical. Proceedings of SPIE - The International Society for Optical Engineering 9127, 91271F (2014).
[16] A. Druzhinin, I. Ostrovskii, Yu. Khoverko, K. Rogacki, I. Kogut, V. Golota Nanoscale polysilicon in sensors of physical values at cryogenic temperatures, Journal of Materials Science: Materials in Electronics 29, 8364 (2018); https://doi.org/10.1007/s10854-018-8847-0.

[17] I.T. Kogut, V.I. Holota, A.A. Druzhinin, V.V. Dovhij, The device-technological simulation of local 3D SOI-structures. Journal of Nano Research 39, 228 (2016); https://doi.org/10.4028/www.scientific.net/JNanoR.39.
[18] M. Masin, M. Kortla Pulsed Deposition vs. Continuous Growth: Monte Carlo Study of Submonolayer Regime, E-J. Surf. Sci. Nanotech 8, 65 (2010).

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Моделювання процесів росту на поверхні кристалів

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У статті розглядаються моделі процесів росту плівок та інших структур на поверхнях кристалів, які мають подібну кристалічну структуру із незначним параметром невідповідності граток речовин, із яких утворені плівка та кристалічна підкладка. Проведений огляд методів моделювання, що основані на аналітичних співвідношення та обчислювальних алгоритмах. Розглянуто ряд методів моделювання найбільш типових процесів: формування поверхні у вигляді пірамідальних утворень (так звані голчасті кристали), двовимірний із початковими острівцями росту та тривимірний нерівномірний процеси росту. Для моделювання процесу росту голчастих кристалів запропоновано використовувати метод, що оснований на гаусовій статистиці приростів висоти поверхні. Розглянуто також модель тривимірного росту кристалічної поверхні, яка використовує ітераційний алгоритм Фосса, і яка дає можливість дослідити процеси ступінчатого, нерівномірного росту кристалів. На противагу ступінчатому росту розглянуто модель субмоноатомного росту плівки, що основана на методі Монте-Карло. Для субмоноатомного росту плівки застосовано псевдовипадкові послідовності, які моделюють початкове розміщення острівців зародження наступного шару на кристалічній поверхні. Визначені обчислювальні характеристики цього методу, а саме залежність числа ітерацій, необхідних для заповнення поверхні цілком, від коефіцієнту початкового заповнення поверхні.

Ключові слова: метод Монте-Карло, ріст кристалів, аналітичні методи.