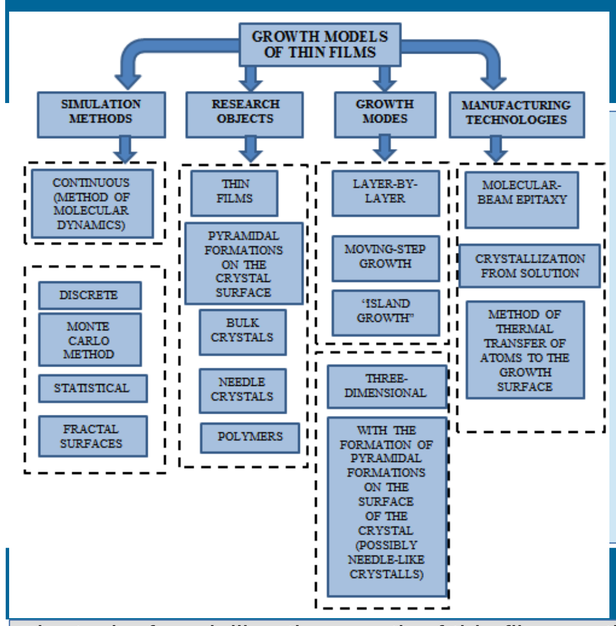
Modeling of crystal growth by statistical methods



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Introduction

The task of modelling the growth of thin films on the surface of crystals remains very important, as it makes it possible to optimize the complex technological process of deposition of film with given thickness and structure. The specificity of the problem of modelling the growth of a thin film on the surface of the crystal has led to a number of theories that somehow explain the mechanisms of the main growth regimes and make it possible to predict which mechanism will be implemented in given technological conditions. Most models of thin film growth can be divided into micro- and macroscopic models. The basis of modern microscopic models is the equation of motion of atoms near the crystal surface in a potential field created by atoms and electrons in the vicinity of the film growth surface **[1]**. But solving this problem is too complicated even for modern distributed computing systems, so macroscopic models are also relevant. Macroscopic models are divided into two main categories: layer-by-layer (two-dimensional) and three-dimensional growth models.

Two-dimensional models can be divided into models based on the growth and fusion of individual islands of growth and the movement of the so-called steps formed by a monoatomic layer along the crystal surface. The first is the mechanism of formation of a new layer by means of islands of growth having random distribution on a crystal surface. This occurs in the case of the same chemical potential of the adsorbed atoms on the crystal surface. This growth mechanism occurs when the kinetic energy of the adsorbed atoms is large enough to move in the plane of the growing layer to take a position in a free node surrounded by atoms of the growing layer. This situation most often occurs if the growing layer is in a semi-molten state. Growth islands can be formed at the stage of pre-treatment of the crystal, for example, isotropic etching, implantation of growth catalysts, the formation of temperature gradients on the crystal surface.

The second mechanism of two-dimensional growth is called "moving step", most often occurs in the process of crystallization from solution. The crystallization process is similar to the motion of a plane filled with atoms in some certain directions. One of the most well-known models that determine the laws of "motion" of the atom-filled layer is the six-vertex model **[2]**.

This mechanism is the least studied from the point of view of modelling, although it is very important from the point of view of surface formation with given reflection coefficients in a wide range of solar radiation **[3]**.

Main references:

1. Pascal Brault. Multiscale Molecular Dynamics Simulation of Plasma Processing: Application to Plasma Sputtering. Frontiers in Physics, Frontiers, 2018, 6, 59 (7 p.).
2. Levi, Andrea & Kotrla, Miroslav. (1996). Theory and Simulation of Crystal Growth. Journal of Physics Condensed Matter. 9. 299-344.
3. 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, No. 102, Art. No 109782, 2020.

Modeling of three-dimensional surface growth

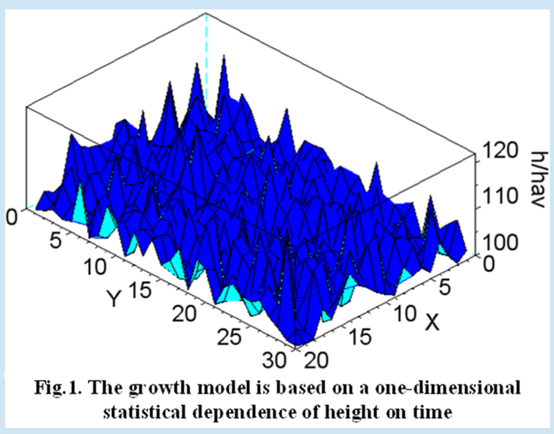


Fig.1. The growth model is based on a one-dimensional statistical dependence of height on time

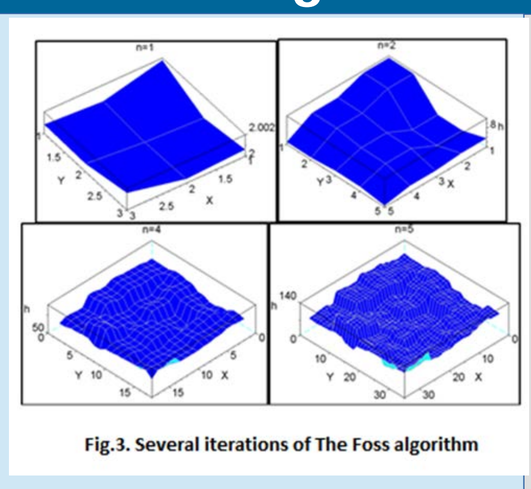


Fig.3. Several iterations of The Foss algorithm

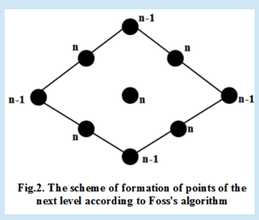


Fig.2. The scheme of formation of points of the next level according to Foss's algorithm

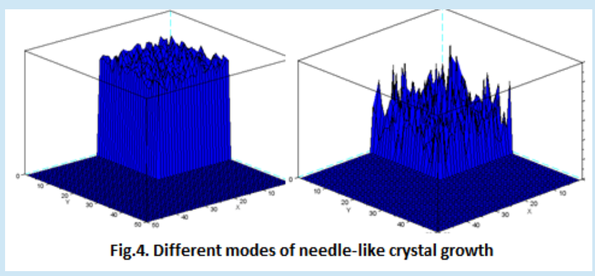


Fig.4. Different modes of needle-like crystal growth

We performed simulations in order to obtain all possible mechanisms of film growth: two-dimensional, three-dimensional and mode with the formation of needle crystals on the growth surface. A one-dimensional model based on the analytical form **(1)** of the dependence of the surface height on time was used to model the growth of needle crystals, the simulation results are shown in Fig.1.

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

In formula (1) c1, c2 are numeric constants, ξ is a random variable with a Gaussian distribution, h is the surface height, and t is time.

We also simulated three-dimensional surface growth by constructing a Foss fractal surface and two-dimensional surface truncation by iteratively adding statistically independent increments for each point, which were also determined by expression *(1)*. The Foss algorithm generates fractal relief in stages, grinding the elementary cell of the grid at each step of the algorithm, as shown in Fig.2. The height of the points of the next level of the fractal surface is determined by the arithmetic mean of the surface heights of the points of the previous level involved in the formation of the fractal surface and some increment, which is defined as a random variable with Gaussian distribution. The result of several of the first five iterations of the algorithm is shown in Fig.3.

By selecting the parameters of the surface construction algorithm based on the Foss algorithm and adding statistically independent increments of the height of the points of the fractal surface, it is possible to achieve high-quality reproduction of different modes of three-dimensional crystal growth (Fig. 4).

Modelling of two-dimensional growth

We have developed and implemented an algorithm that simulates the mechanism of two-dimensional growth of a crystal film of a simple cubic structure using an island mechanism. 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 in the total number of elements of the matrix is one of the main parameters of the simulation, which is associated with the corresponding technological parameter of film growth. The condition of filling the film layer in the free node is determined by the interaction potential of the adsorbed atoms, atoms and electrons of the crystal. In the simplest case, the interaction potential depends only on the number of nearby neighbouring atoms or vacancies to a particular node.

In the simulation, the condition of filling the film layer in a particular node is determined by the number of filled nodes closest to it. That is, if the number of filled nodes exceeds or is equal to half of all nearest, then in this node the top layer is formed. For nodes in the corners of the matrix, this means that the upper layer is formed if more than one node is already filled, for nodes located on the sides of the square (crystal face), the upper layer is formed if more than two nodes are filled in the next layer, and for nodes inside the crystal, the growth of the next layer occurs if more than the nearest four nodes are filled. The simulation is performed for values of initial filling coefficients acceptable from the point of view of film growing technology: from 13 to 25%. The lowest value of the fill factor determined using the developed model is 13%. At this value, a statistically acceptable level is observed (out of 20 different initial fillings selected at random in 15 cases, the top layer is filled completely in less than 100 iterations).

In fig. 5 shows the results of modeling the process of two-dimensional film growth for the initial filling coefficients of 11%, 18% and 25%. The dependence of the number of iterations required for film formation on the initial filling factor, which is shown in Fig.6, is investigated. Calculations are performed for 20 randomly selected initial fillings of the growth surface.

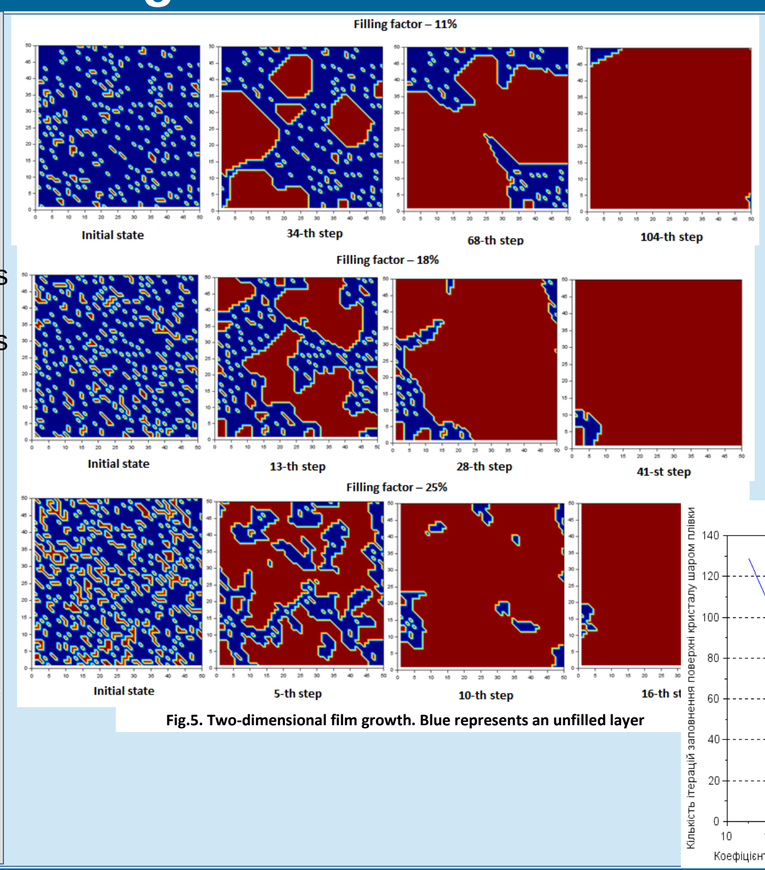
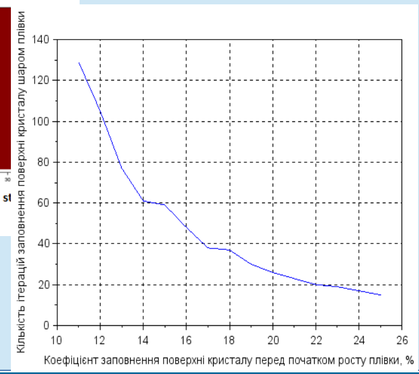


Fig.5. Two-dimensional film growth. Blue represents an unfilled layer



Main results and conclusions

The paper reviews the main growth models associated with the actual modes of growing thin films. Based on the analysis of analytical and statistical methods, multiparameter methods for modelling the three-dimensional mode of surface growth have been developed, which reproduce two-dimensional and three-dimensional modes of growth of thin films. It is shown that on the basis of Foss's algorithm, supplemented by analytical methods, it is possible to achieve high-quality reproduction of needle crystal growth process, for which modelling methods are the least developed, but which are of great practical importance for growing surfaces with given optical properties.

A model of two-dimensional surface growth is also developed based on two basic rules: random distribution of growth islands on the crystal surface, and determination of the number of filled nodes that are closest to this. This model is of great practical importance for the selection of the most important technological parameters and can be adapted to real film and substrate materials by selecting the interaction potentials of atoms, which affects the probability of major processes on the growth surface: absorption, evaporation and diffusion.