

09. SELF-REFERENCE on the scientific contributions of assoc. prof. Bogdan Ranguelov (IPC, BAS), based on all scientific papers

The self-reference is based on 41 scientific papers (referred in Scopus), published between 1999 and 2020. List of these 41 scientific papers is given as document number 8 in the documents file. Overall, the papers could be categorized within the scientific field of electron microscopy (fundamental and applied) studies and computational simulation studies of phase formation in condensed matter physics. The chronological tracking of all papers highlights the sub-fields of (main) interest, and of course, shows both some "momentary interests" and the search for new challenges in specific scientific problems. The grouping of all scientific papers can be done in the following areas and sub-areas, taking into account that some paper could be connected to more than one scientific field:

Scientific field I: Electron microscopy studies of phase formation in condensed matter physics

I.1. Electron microscopy studies of 2D nucleation, crystal growth (homoepitaxy) and instabilities on vicinal crystal surface Si (111).

I.1.1. Two dimensional nucleation, crystal growth (multilayer island and spiral) and critical terrace width on vicinal crystal surface Si (111). [4, 16, 20, 27]

I.1.2. Instabilities on vicinal crystal surface Si (111) – step density waves. [29]

I.2. Electron microscopy studies of phase formation and characterization of glass and glass-ceramics materials, soft condensed matter, thin films and catalysis.

I.2.1. Glass and crystal-glass materials. [14, 15, 17, 25, 30, 32, 36, 40]

I.2.2. Soft condensed matter. [22, 37]

I.2.3. Thin films and catalysis. [1, 2, 3, 11, 13, 21, 26, 31, 33, 34, 41]

Scientific field II: Simulation and theoretical studies of phase formation processes in condensed matter physics

II.1. Simulation and theoretical studies of surface instabilities on vicinal crystal surfaces

II.1.1. Step density waves instabilities – non-stationary BCF model, electromigration and step permeability. [7, 8, 10, 29]

II.1.2. Step bunching on vicinal crystal surfaces. [5, 12, 18]

II.1.3. Critical terrace width for step flow growth mode and 2DN and step permeability. [6, 9]

II.2. Monte Carlo computer simulations on adatom diffusion on vicinal crystal surfaces and step permeability. [9, 23, 24, 38]

II.3. Monte Carlo computer simulations on thermal stability of metal nanowires [28, 35]

II.4. Monte Carlo computer simulations on patchy particles and two particles DLA model. [39, 19]

The main contributions according to the above fields and sub-fields of scientific interest and research can be summarized as follows:

I.1.1. Two dimensional nucleation, crystal growth (multilayer island and spiral) and critical terrace width on vicinal crystal surface Si(111). [4, 16, 20, 27]

Reflection electron microscopy (REM) is used to study the spiral mechanism (growth or evaporation) on vicinal crystal surface Si (111) for temperatures above 830 °C (the temperature for phase transition $(7\times 7) \leftrightarrow (1\times 1)$). Modification of the position of the recording camera, the so called LODREM mode (low distortion reflection electron microscopy) is used, thus for the first time we have acquired non-distorted images of monatomic spirals on Si (111). The distortion of the images in REM is due to the low angle electron beam interaction with the sample surface and as a consequence the images are shortened fifty times in one direction. The distance between two consecutive spiral turns is the main parameter under investigation in both growth and evaporation conditions at different temperatures and different super/under saturations. This parameter is fundamental for the “classical” BCF model of spiral growth. Here and hereafter, by “classical” BCF model we will assume the notion that adatoms on the vicinal crystal surface diffuse until they re-evaporate or until they incorporate in a kink site of a step – thus the steps “collect” the adatoms and there is no mass transfer of adatoms across the steps. In this case there is an inverse proportionality (exponent 1) between the distance of two consecutive spiral turns and the supersaturation – this is the so-called “local steps dynamics” without overlapping of the step diffusion fields. For both cases of growth and evaporation the relation between the distance of two consecutive spiral turns and the super/undersaturation is inverse proportional, with an exponent that differs from 1, namely between 1/3 and 1/2. This is the main result, that reflects the overlapping of diffusion fields from adjacent steps, due to the large diffusion length of the adatoms in this particular temperature interval, the back-stress effect, as well as the fact, that the steps are reputed to be “transparent” (or permeable) for some of the adatoms. By transparent (or permeable) steps here and hereafter we will accept the notion that an adatom could cross a step without incorporation, thus there is a mass transfer between two adjacent terraces, divided by a monatomic step.

The processes of homoepitaxy on vicinal crystal surface Si (111) are studied by REM in 3 publications [16, 20, 27], and we have used the theoretical predictions in [6, 9], thus bridging the theoretical/simulation investigations and the experimental one. This bunch of papers is based on an experimental attempt [29] for evidence of the predicted instability of a new type, namely the so called step density waves instability on vicinal crystal surface.

The main subject of these studies is the so called critical terrace width – the width at which the step flow growth mode is switched do 2D island growth mechanism on the terraces. All experiments are performed below the temperature of $(7 \times 7) \leftrightarrow (1 \times 1)$ phase transition, on preliminary created wide atomically smooth terraces (by high temperature step bunching). Different temperatures are used (by DC heating) as well as different incoming flux of Si adatoms from gas phase. At late times of homoepitaxy, we find that the mechanism of growth is multilayer, forming dynamical pyramidal structures with space and time periodicity. It is shown, that there is a critical temperature of 720 °C, below which the crystal growth is attachment (kinetically) limited, while above 720 °C the crystal growth is diffusion limited. The scaling exponent between the critical terrace width and impinging flux of adatoms is calculated, which is used for determination of the critical nucleus size and the activation energies for 2DN below and above 720 °C. This experimental results are connected and linked with the theoretical and simulation results [6], thus this allows us to calculate the value of the ES barrier. Additional investigations by AFM resolved the different step edge morphologies (step roughness below and above 720 °C), thus they are linked to the specific peculiarities of attachment and/or diffusion growth regimes.

The same experimental setup is used to study the so called „step permeability” and its connection with the pyramidal growth structures and their morphology, depending on the balance of adatom fluxes diffusing in step-up or step-down direction. [27]. Detailed studies of the 2DN and growth on the upper most terrace of the pyramidal structures revealed the discreet mechanism of the balance between the two diffusion fluxes. We use wide Si (111) terraces (between 1 to 100 mkm). In the temperature interval 600 – 750 °C we show that the continuous 2DN and growth results in pyramidal prolonged wave structures (at $T < 720$ °C) and separate pyramidal structures (wedding cakes type) at $T = 750$ °C, and both structures reflect an instability during crystal growth. These instabilities are result of the slight difference between the adatom fluxes crossing the steps in step-up or step-down direction, the relative high ES barrier and the density of kinks at different crystallographic orientations. The change (shortening) of the upper most terrace width of the pyramidal formations, as well as the increasing of the number of terraces forming them, are clear indications for increasing of the size of the critical nucleus and a corresponding adatom flux of adatoms in step down direction at $T = 650$ °C. However, at $T > 720$ °C we indicate an increased flux of adatoms in step up direction, because of the increased ES barrier for incorporation in the upper step. Here, it is worth to mention, that the higher barrier ensures much longer life time of the adatom onto the step edge, thus increasing the “chance” for crossing the step, which is in fact increasing the probability for a permeability event. This slight advantage in the value of the step up adatom flux leads to the so-called second layer nucleation and it is responsible for the switch of the growth morphology from elongated pyramidal wave forms to separate (individual) pyramids.

I.1.2. Instabilities on vicinal crystal surface Si(111) – step density waves. [29]

This work provides an experimental evidence on the theoretical and simulation studies in [7, 8, 10]. They are based on the assumption of non-stationary solution of BCF type equations for step motion on (1+1) D vicinal crystal surface – diffusion equations for the adatom

concentration on the terraces and boundary conditions on the steps confining the corresponding terrace. Both theoretical and simulation studies show that at specific conditions (high impinging flux of adatoms, high speed of steps) in kinetic regime (fast adatom diffusion on the surface and relatively slow attachment/detachment to/from the steps) the crystal growth will be unstable, even if there isn't destabilizing factor/force (contrary to the case of step bunching, where the destabilizing factor could be the electromigration force, ES barrier or even some impurities on the step edges – more details in II.1.1.). Concerning the experimental setup, it is a challenge to manage the proof of this newly kinetic type of surface instability, namely to find the conditions at which without any destabilizing factors one could use the REM experimental technique. The studies are performed on vicinal crystal surface Si (111), which is reputed to be extremely suitable for such experiments, due to the high value of the equilibrium concentration of adatoms. The crystal is heated by applying a DC current. We use the REM microscopy technique in a suitable and wisely chosen temperature interval as well as current direction, at which the electromigration force acting onto the adatoms doesn't cause step bunching instability – contrary, our experimental results show the initial stages of formation of the so called step density waves instability during growth conditions at maximal achieved flux of adatoms of five bilayers per second. The observed instability (step density waves) could exist until the value of the adatom flux coming from the gas phase is still enough (overcritical) in order to provoke the non-stationary effects [7].

I.2.1. Glass and crystal-glass materials. [14, 15, 17, 25, 30, 32, 36, 40]

This is a significant, interesting and important part of our research, most of which was conducted by the group of glass and glass-ceramics at IPC, BAS [14, 15, 17, 25, 30, 36]. In some of these studies, my contribution is generally smaller compared to studies on other topics mentioned in this reference. In [14, 15, 17, 25] the problem of treatment of specific waste raw materials after their processing by an incinerator and their use as a significant part (up to 60%) of the raw materials for obtaining sintered glass-crystal materials is considered. After obtaining the so called frit (glass powder/grains), it is pressed and subsequently sintered at different temperature regimes – temperature heating gradients and constant temperature steps. Different initial raw fractions could be used after filtering. The thermal shrinkage of the newly obtained materials, their density, water absorption, surface and fracture morphology, structure, elemental and phase composition, determination of a separate crystalline phase, as well as the influence of an inert sintering atmosphere were studied. Special attention is paid to the so called open and closed porosities. It is worth to mention that the so called microporosity (pore size below 5 μm) is not related to “defects” in the material, since it is connected to enhanced mechanical parameters. Last but not least, the possible positive environmental impact of this research must be taken into account. My contribution in these works is mainly in electron microscopic research, which in turn has led to a better acquaintance and study of amorphous materials in general on a personal level. In [30, 36] the preparation and characterization of glass-ceramics obtained by immobilization of large quantities of metallurgical waste (mainly iron oxides) - from the production of steel and ferronickel are considered. Iron oxides can play the role of nucleating agents (centres) and to favor

crystallization processes during the heat treatment of the parent glass. The processes of nucleation in the newly obtained materials were studied - the optimal temperature was determined, as well as the retention times for obtaining the crystalline phase. In the study of glass-ceramics obtained from waste products from steel production, the formation of crystallization-induced porosity during bulk crystallization was proved. It was found that the main structure of glass-ceramics obtained from wastes from the production of ferronickel is the result of liquid-liquid separation, which leads to the formation of a very fine crystalline magnetic phase, which "serves" as a "substrate" for the growth of the main pyroxene phase in the newly obtained material.

Manuscript [32] is based on synthesis of $ZnTeO_3$ during crystallization from composite system Te-Bi-Zn-Nb. My contribution in this study is in the electron-microscopy observations. In [40] the influence of the Fe^{2+} / Fe^{3+} ratio on the properties of the Mg-Al-Si-O system was studied. This is a task developed and considered together with colleagues from Aveiro, Portugal, in obtaining the material using the so-called „laser melting in the transition zone“- Laser Floating Zone technique for obtaining glassy and crystalline materials. The main research is related to measurements of the conductivity and magnetic properties of the obtained materials. My contribution to this work is both in electron microscopic research and in the overall design of the experiment and the "construction" of the research team.

I.2.2. Soft condensed matter. [22, 37]

In [37] my contribution is in the study of the structure of adsorbed layers of two-anten oligoglycines (joint work with the department of colloid systems, IPC) on different types of substrates (wetting / hydrophobic effect) and different concentrations. A wide range of structures with specific morphology has been obtained - from dense coatings, through mesh, composed of rod-shaped, elongated or plate-like complexes.

In [22], a study of the antibacterial effect of ion-exchange clinoptilolite on *Escherichia coli* was performed. The antibacterial effect for the case of ion-exchange clinoptilolite with Ag and Cd is shown.

I.2.3. Thin films and catalysis. [1, 2, 3, 11, 13, 21, 26, 31, 33, 34, 41]

In these works, studies on thin films and catalysts are generally collected. In this group are my first two serious publications [1 and 3], in collaboration with colleagues from IPC. Of course, in these two works as a young scientist (and in some other earlier works in this field) I can not have a very significant contribution, but I learned/saw a professional attitude to a treating of scientific problem, as well as to the creation/writing of a publication [3]. In [1], thin films (coatings) of CdS deposited on ZnO and ITO glass substrates were investigated by electrodeposition from a melt (temperatures above 400 ° C), varying both the current density and the deposition times. In [2], the electrochemical incorporation of Cu (copper clusters) into polyaniline (thick) layers on a Pt substrate was studied, paying attention to the anodic oxidation peaks (potentio-dynamic curves) at different thicknesses of the PAN layers. There are three "places" of deposition of copper clusters depending on the defect in and on the oxidized state of the layers.

In [3] the morphology of the obtained carbon structures (with built-in iron) is studied, as a result of a process of growth far from equilibrium - the arc between two carbon electrodes is an atmosphere of Ar and ferrocene. Various carbon (nano) structures of the anode and cathode were obtained - nanotubes of different length and size, balls of nanotubes and cone-shaped formations. In [11] my participation is more like as a technical staff. The works [13, 26] are in collaboration with colleagues from FTM, Skopje and are related to extended studies of nonstoichiometric phases of TiO_2 , as a "carrier" material (thus the use of platinum is avoided) for cobalt catalyst for HER / OER evolution reactions – the influence of the preliminary mechanical processing (in order to increase the active area) of the material with the trade name Ebonex. The contributions in this work are related to the combined microscopic examination - transmission and electron microscopy. The so-called sol-gel method for TiO_2 synthesis using TTIP precursor and by "simple" laboratory conditions. After the heat treatment, the anatase / rutile phases are obtained. The morphology of the obtained phases / aggregates, the shape and the sizes of the obtained nanoparticles are characterized by transmission and electron microscopy.

In [21] I participated in the study of thin molybdenum films on steel obtained from the "sintering" of molybdenum trioxide powder using a laser beam. The process of amorphous phase formation and recrystallization depending on the beam parameters (duration, direction) as well as the temperature was studied.

The cycle of works [31, 33, 34] is a result of cooperation with CLAP-BAS, Plovdiv and considers mechanical and structural features of titanium and chromium hard coatings obtained by unbalanced magnetron sputtering and cathodic-arc sputtering. The optimal annealing temperature for obtaining high hardness CrTiAlN coatings and modulus of elasticity was determined. The influence of the nitrogen flow on the mechanical properties of the Ti / TiN / TiAlCrN and Cr / CrN / CrTiAlN coatings was also studied. Multilayer TiN / ZrN coatings were also investigated. My contribution to these works is related to electron microscopic observations and the preparation of experiments.

II.1.1. Step density waves instabilities – non-stationary BCF model, electromigration and step permeability. [7, 8, 10, 29]

This is a cycle of four publications, first three of them are prepared in a relatively short interval – these are the works in which the notion and whole idea of the so called step density waves type of instability is presented. The fourth publication is based on the experimental evidence of the step density waves instability on Si (111). I should note that it was the search for such experimental evidence that led to the development of another interesting (experimental) topic discussed in [16, 20, 27]. The considered system is a vicinal crystal surface, in which we have monatomic steps, separated by atomically smooth terraces. The process of crystal growth (or evaporation) takes place by step flow mode, ie. adatoms join (or separate from) the steps, effectively leading to movement of the steps and to a crystal growth (or evaporation) as a result. The 2DN on the terraces is ruled out. The publications [7, 8, 10] are based on the following question: what will happen during the process of crystal growth / evaporation, if the

step propagation velocity is significant higher? Here by “significant higher” velocity, we have in mind such velocity, that the stationary conditions are no more fulfilled, and then the adatom concentration on a terrace depends on time (and not only on the position, like it is in the stationary case). Since the diffusion equations are of second rank (and it is not so easy to integrate them), we use the notion of the kinetic regime at which there is a fast diffusion onto the terraces and thus the adatom concentration is constant. In this way the problem could be solved by splitting the equation with two variables to two equations with one variable of first rank – one equation for the adatom concentrations and one equation for the terrace widths, and of course the two systems of equations are coupled. To determine the evolution over time of the system of steps, we examine how the widths of the terraces that are located between the steps change with time. This is done by numerically integrating the equations describing the widths of the terraces by the Runge-Kuta method. The essence of the considered model is that the concentration of adatoms on a given terrace is constant over the whole terrace (fast diffusion), but it depends on whether in a previous moment this terrace was "wider" or "narrower". If the terrace in its "past" was wider, then the concentration of adatoms (now) will be lower, and vice versa - the concentration of adatoms will be high, if in its "past" it was narrower. Here is the place to mention that in a real experiment a vicinal surface can never be achieved at which the monatomic steps are equidistant, i.e. separated by terraces of equal width. Since the distances between the steps (the widths of the terraces) are different initially (even if we assume that they have a small difference), in the process of growth or evaporation, depending on many factors, the system can equalize all the distances between the steps (this is stable growth or evaporation), or where the distances between the steps were smaller to become even smaller and where they were larger to become even larger (this is unstable growth in which the system of steps “breaks down” into groups (bunch) of steps very close to each other and wide terraces between the groups. In this case, it is shown that such instability can occur in the absence of any (external) destabilizing factors, but only due to the effects of non-stationarity. In [7] the grouping of steps in non-stationary solution of the BCF model in kinetic limited mode was studied, as the found effect (the conditions under which we have an unstable solution of the system) is called “kinetic memory” on the widths of the terraces. The numerical integration of the system of equations (under conditions of instability) shows that waves of compression of the density of the steps will propagate along the vicinal crystal surface. In [8], the considered model is complicated by the addition of one factor, which in many cases cannot and should not be neglected - this is the so-called electromigration force - the force that acts on the adatoms on the surface of the crystal, if a DC flows through the crystal. The conducted linear stability analysis shows that now, taking into account the influence of electromigration force, the system can be unstable both due to the already considered kinetic effect of the memory of terraces and due to the influence of electromigration when the force has a certain direction and value. The natural continuation of the model considered so far is to introduce the influence of the transparency of the steps - this means that the speed of a step at a given time will depend on processes (jumps) that occurred on "more distant steps" in previous moments [10]. This is exactly the so-called "non-local" dynamics of the steps, discussed above [4] and which is also studied in [9] by the Monte Carlo method. In non-local dynamics, adatoms need time to cross a number of steps before joining the crystal in the kink position. The vicinal surface with transparent steps is unstable when the

drift velocity of the adatoms multiplied by the relative change of the adatomic concentration from the equilibrium is greater than the critical velocity for the movements of the steps.

II.1.2. Step bunching on vicinal crystal surfaces. [5, 12, 18]

These are a series of model studies on modified equations of the BCF type, with different model parameters included (or excluded), and the aim is to find the conditions for instability under which the steps on a model vicinal surface will not be equidistant, but will form the so called step bunches. In [5 and 12] the main prerequisite for destabilization of the system of steps is the introduced difference in the equilibrium adatomic concentration on both sides of the steps - here it must be emphasized that these are nonequilibrium processes in which such an assumption can be justified. The position of the minimum distance between the steps (the steepest slope of the surface) in a group, as well as the dependence (degree) of this distance on the number of steps in the bunch were studied. The scaling relations between the size of the groups of steps (the number of steps in a given group), the width of the whole group and the time are obtained. In [18], two models of step flow mode were studied, in which the speed of a given step is determined by dependences which include only the widths of the adjacent terraces. These models seem to be abstractly constructed, but manage to recreate some of the characteristics of the considerable variety of experimentally observed step bunching - groups of steps in which the slope of the group is constant, or those in which the slope increases.

II.1.3. Critical terrace width for step flow growth mode and 2DN and step permeability. [6]

Again, the model system is a vicinal crystal surface, ie. a large number of monatomic steps, which are separated from each other by smooth terraces. Both [6, 9] combine the efforts to understand the phenomenon of transparent/permeable vicinal steps and their impact on the morphology of growth and in particular the transition from step flow growth to 2D nucleation on the terraces. The mechanism of growth by step flow mode takes place when the temperature of the crystal surface is high enough so that the free diffusion path of the adatoms is greater than the average width of the terraces. Lowering the temperature leads to increasing of the probability for formation of a critical nucleus and thus the formation of 2D islands on the terraces and a corresponding new growth mechanism. Which one of these mechanisms the system will chose – this is ruled by the terraces widths on the vicinal surface, and the transition between the two mechanisms is exactly at the so called critical terrace width for a given temperature. In [6] we present a general model, including the asymmetry of the kinetic coefficients for adatom incorporation to the steps (every terrace is bounded by two steps) and the corresponding step permeability/opacity. The evaporation is ruled out, thus all the adatoms on the vicinal surface sooner or later will join (somewhere) at the steps. A general equation for the adatom concentration on the vicinal terrace is obtained, the ES barrier and step permeability is under consideration. Increasing the asymmetry leads to a shift in the maximal value of the adatom concentration, while increasing the step permeability minimises the effect raising from the asymmetry in the kinetic coefficient. A general equation for the critical terrace width is obtained, considering the asymmetry in the step coefficients and the

step permeability. An Arrhenius dependence of the critical width of the terrace with decreasing the temperature is obtained, as the dependence itself represents a smooth transition between two lines with different slopes (two regimes), corresponding to the two regimes of growth - diffusion limited and kinetically (attachment) limited (see also the experimental results in [20]). An evaluation of the transparency of the steps vs. temperature shows that the “transparency” is greatest in the so called “average temperature” range/interval between the “pure” kinetic and “pure” diffusion regimes. This theoretical consideration is compared with the experimental data on the critical width of terraces for Si (111) (7x7) by other authors (LEEM microscopy), from which the existence of an inverse Ehrlich-Schöbel barrier was found and the binding energy of 3 -atomic critical nucleus was calculated.

II.2. Monte Carlo computer simulations on adatom diffusion on vicinal crystal surfaces and step permeability [9, 23, 24, 38]

These studies present Monte Carlo simulations of diffusion processes of adatoms and atomic clusters (or islands) and related phenomena, such as the transparency of steps and the change in the shape of clusters (islands) under the action of electromigration force. In [9] another aspect of the problem treated in [6, 10] is considered, namely – if we assume that we have an “non-local” step dynamics, and that the adatoms could jump/cross across the steps, so how big (as area or number of steps) is this “non-local” step dynamics? Or, how many steps an adatom may “visit” before its incorporation into a step. A relatively simple model of a vicinal surface is considered - a square lattice with one “central (zero number)” terrace, and other similar terraces (unlimited number - during the periodic boundary conditions and taking into account the number of their “position”), which bear positive consecutive numbering if up the steps or negative consecutive numbering if they are down the steps (compared with terrace number zero). All steps on all terraces have the so called kink sites, and their density (step roughening) is a model parameter. An adatom is placed on the zero terrace, then it begins to make a random walk on the square lattice, and when it reaches the step edge, it can diffuse along the edge, detach from the step and return to the terrace from which it came, or to jump over the step and go to the upper or lower terrace (permeability event), respectively, and for each of these processes some probability is set in advance. The electromigration force acting onto the diffusion of adatoms is also considered (biased diffusion). It is shown that in the absence of electromigration force and in the absence of the Ehrlich-Schöbel barrier, we have symmetrical (histograms) to the central (zero) terrace of the distribution of the number of jumps over the steps higher or lower than the zeroth terrace. The main result here is, that by varying the parameters of the model, such as the density of kinks on the steps, or the probability of diffusion on the edge of the steps, in all cases (averaged) an adatom visits up to 10 steps in the vicinity of the terrace from which it began its diffusion (after accommodation on the surface from the gas (parent) phase). This is an important result even based on a simplified model. The presence of asymmetry in the attachment of adatoms to the steps on both sides of the terraces (Ehrlich-Schöbel barrier) drastically reduces the transparency of the steps (the sum of all probabilities for possible elementary processes is one), but the histograms of the number of jumps across the steps remain symmetrical. It is shown that there is a scaling relationship

between the average number of jumps “performed” by an adatom and the average distance between kinks on the steps. If we include in the model the action of an electromigration force that “pushes” the adatoms in a given direction (perpendicular to the steps), then there is a strong “stretching” of the histograms in the direction of the force (analogous to the Pearson distribution family). It is shown that even a very small value of electromigration force has a dramatic effect on the diffusion trajectory of an adatom - the reason is that the adatom makes a large number of “attempts” to jump and eventually even a small value of electromigration force begins to matter. Here, of primary importance is the result, which shows that even with bigger electromigration (external) force, the number of steps that are crossed by an adatom does not exceed 10 - 15, which again indicates the area of “non-locality” of the dynamics of the steps. The main conclusion of this work is that even if we have transparency of the steps, the speed of movement of the steps should not change, because sooner or later all the adatoms will join one of the steps, even if it is not the first which they encounter.

In [23] and [24] we consider the diffusion of adatoms on a model terrace with orientation (111), using the so-called tight-binding potential and Metropolis Monte Carlo algorithm. In [23] the stability (integrity) of a monatomic two-dimensional island on the surface is considered, taking into account the action of an external force (electromigration) on the atoms of the island. The balance between normal, lateral and external forces acting on the island's atoms also determines the critical values of the external force at which an initially compact island evolves: three values of external force are defined in terms of morphological stability of the island - at low force (only 1.5% of the strength of the interaction between the atoms of the island) the separation of single atoms from the periphery of the island is observed, but in general the integrity of the island is preserved. As the external force increases, the original single island breaks up into individual smaller islands, while an even greater increase in external force leads to the complete disintegration of the island into individual adatoms. Here it is important to note that the transition between these three regimes is not smooth, but rather abrupt.

The same physical model was used in [24], where the influence of the density of kinks on the steps on the transparency of the steps was studied, taking into account the action of external electromigration force. These studies offer a possible scenario and model to explain the “mystery” of the complex behavior of the phenomenon of grouping of steps on the Si surface (111) depending on the direction of electromigration force and temperature. The model is generalized as it generally refers to adatoms on a terrace fcc (111), without taking into account the specifics of silicon (Si). It has been experimentally proven that for the Si (111), there are three consecutive temperature intervals in which grouping (bunching) of steps (instability) alternates with stable growth (lack of grouping of steps). Theoretically (in the frame of BCF model) such “switch” from stable to unstable and reverse to stable growth mode could be explained if only the transparency of the steps is assumed. This paper proposes a generalized scenario that can explain why steps can “switch” sequentially from impermeability to permeability and back to impermeability. In the considered model we have adatoms, which, in addition to thermal diffusion, also perform directed diffusion under the action of an external (for example, electromigration) force. This force acts (only) on the adatoms in a direction perpendicular to the step. It has been shown that at a relatively low temperature (lower than the roughing temperature of the step) and a relatively small value of the external force, the

step remains almost smooth (no thermal kinks are formed) and the adatoms cannot jump / cross the step, but decorate the step ledge. At the same temperature, but at a higher values of the external force, the adatoms can now cross the step, ie. to move to a higher terrace. However, as the temperature increases and when the roughing temperature is reached, the formation of kinks on the step edge begins to act as a "trap" for the adatoms and as a result the step begins to become increasingly impermeable. With an even greater increase in the temperature (but of course far below the melting temperature), the steps can again become transparent for the adatoms, which is due to the high temperature thus they would have enough thermal energy to overcome the step edge barrier and with the "help" of the external force to manage to cross it. This is a relatively simple model, but it shows the relationship between the temperature, the roughness of the steps, the external force acting on the adatoms and their overall relationship to the phenomenon of step transparency (permeability). In [38], the kinetic Monte Carlo method was used to study the directed biased diffusion of two-dimensional islands and voids on a (111) surface. Biased diffusion is the result of the action of an external force, and in most cases such studies take into account the electromigration force as an external one. In this simple model we use an infinite Ehrlich-Schöbel barrier, ie. atoms cannot jump over/cross the steps. In this sense, the model is completely two-dimensional. The main results are related to finding the change in the shape of the initially equilibrium two-dimensional islands or voids clusters, as a result of the directed action of the external force.

II.3. Monte Carlo computer simulations on thermal stability of metal nanowires [28, 35]

These studies present Monte Carlo simulations of the thermal stability of metal wires, for the case of free-standing one-dimensional monatomic chains [28] and for the case of "thicker" two-dimensional (flat) homoepitaxial chains on the surface fcc (111) [35]. A tight-binding potential with parameters for copper (Cu) and Metropolis Monte Carlo algorithm was used and the thermal stability of the chain was investigated, i.e. how long it will remain intact and finally break. It is important to note that the only reason for the loss of stability are the thermal fluctuations of the atoms of the metal wire. The break scenario begins with the appearance of vacancies (atoms that are distant from each other on a lattice parameter) and which do not recover and which eventually lead to the appearance of holes in the chain (atoms that are distant from more than one lattice parameter), after which the wire breaks up into separate clusters. Furthermore, it is important to point out, that the wire is free standing in space, and there is an absence of the stabilizing effect that could come from a surface (substrate) [35]. Special attention is paid to the study of the lifetime of the wire (the time until it breaks up) depending on the strength of the interaction between wire atoms. It turns out that (at a given temperature) the chain stabilizes (remains intact for a longer time) by reducing (of course to some reasonable degree) the strength of the interaction between the atoms. This strange result at first glance has its explanation - the reduction of the force of interaction between atoms increases the flexibility of the chain, thus allowing some atoms to occupy places that are not exactly on one line (axis of the chain), and as a result the wire shape appears as standing waves (fluctuations), but in fact exactly they lead to a longer lifetime.

In [35] we consider a similar problem, but already concerning two-dimensional homoepitaxial bands of atoms (these bands are actually several adjacent one-dimensional chains) on a surface (111). The mechanism of their rupture is studied only under the action of thermal fluctuations (no external force). The mechanism of rupture goes through the stages of initial thinning of the strip to the formation of a section with a one-dimensional chain, the formation of vacancies, which, however, can be filled again, but after a long time a "hole" in the strip emerges, which can not be filled, which ultimately leads to rupture and entire disintegration of the strip. Of course, increasing the width of the strip (the number of chains involved in it) leads to a sharp increase in the lifetime of the strip itself, and in this case even a cluster of vacancies can be subsequently filled and so the strip can be "restored".

II.4. Monte Carlo computer simulations on patchy particles and two particles DLA model [39, 19]

In [19] an extended model of diffusion-limited aggregation is considered (based on the original model of Wheaton and Sander, <https://doi.org/10.1103/PhysRevLett.47.1400>). Unlike the original model, here is proposed the introduction of the so-called coefficient of attachment – or sticking coefficient (to the growing two-dimensional cluster), thus we can "shift" the process from diffusion-limited to kinetically (attachment) limited one. The sticking coefficient "represents" the probability for an "atom/particle" to stick/join the growing cluster. If this coefficient is low, then this means that the atom has much more chance to reach the interior branches of the growing fractal cluster. The calculated fractal dimensions reveal the so expected change in the cluster density. The notion of „ giving a chance lower than unity “, for joining the growing cluster is exploited in the second part of the manuscript, where we introduce a model for DLA in a system with two types of particles (named A and B), and A can attach only to A, while B can attach only to B type particles. Main feature of these model is that, if particles A or B, released somewhere from the circumference of the growing cluster and if they diffuse far away from the cluster, then they will be released again from the same starting place. Thus, in this model we can give second, third and so on chance to the particles until they reach the growing cluster and until they attach to it. This, one may say artificial scenario, leads do growing spiral fractal aggregates.

In [39] the most recent simulation studies are reflected, in which "softer" condensed matter and interactions between model molecular complexes are considered, which are not spatially symmetric, but are directed - this is the so-called patchy particle model (Doye model - <https://doi.org/10.1039/B614955C>). Patchy particles (molecule complexes) are indestructible and can interact with each other only through their patches - thus introducing direction in the interactions, depending on the specific geometric arrangements of the patches. A modified Doye model is proposed in [39], in which we consider two types of patches (A and B, with only A-A and B-B interactions allowed) and in addition the interactions can differ both in their strength (depth of the potential) and its spatial orientation - the spatial extent to which two identical patches of different particles interact depending on their mutual orientation. A model was chosen in which we have carrier particles (so-called monomers), which are "decorated" with two pairs of patches (each pair is spaced 60 degrees apart and the pairs are symmetrical to each other on one axis). In addition, one pair of patches interacts with their counterparts

through a stronger but spatially narrower potential, while the other pair of patches are weaker but spatially wider (in the sense of an 2D angle). It is shown that there is a narrow temperature range in which a polymorphic structural transition between the rhombohedral phase and the tri-hexagonal (Kagome type) phase takes place. The reason for the observed transition is in the kinetics of formation of the two phases - first the more unstable rhombohedral phase is formed, which serves as a "reservoir" and slowly gives off its building blocks (monomers), which form initially stable trimmers (three monomers rotated mutually at 120 degrees so that all their strong connections are directly opposite each other and thus minimize the energy of the system), and which subsequently form a stable three-hexagonal phase. A detailed analysis of the kinetics of formation of the two phases, as well as the elementary processes of phase construction, the influence of temperature and the anisotropy of the interactions is performed. These studies are currently being continued to simulate the co-crystallization processes of two different types of patchy particles.