REVIEW

**in competition for the academic position Professor
of professional direction 4.2. Chemical Sciences
and scientific specialty "Physical Chemistry",
for the needs of Laboratory "Electron microscopy and microanalysis" of IPC BAS,
on the topic "Electron microscopic and simulation studies
of phase formation processes in condensed matter",
announced in SG Issue No 20 dated 10.03.2020
and with candidate Associate Professor Dr. Bogdan Stavrev Rangelov
Reviewer: Professor DSc. Stephan Atanassov Armyanov**

1. General and short biographical data of the applicant.

In the field of material science, it is difficult to find a complex study that does not involve electron-microscopic analysis, applying very often several of the associated methodologies. The popularity of simulation research is growing with the improvement of computer equipment. The interest in phase formation and crystal growth is traditional for IPC BAS. All this quite briefly justifies the topicality of the theme of this competition.

Bogdan Stavrev Rangelov was born on July 16, 1970 in Sofia. In 1988 he graduated from the Sofia Mathematical High School, profile physics, and in 1995 - The Faculty of Physics of Sofia University "St. Kliment Ohridski", becoming a Master of Physics. In 2009 at IPC BAS B. Rangelov defended a doctoral thesis on the topic: "Instability of vicinal crystal surfaces – grouping of steps". He is an Associate Professor at IPC BAS since 2011. Since 2010, he is Head of the laboratory of electron microscopy and microanalysis of the same institute. Since 2019, he is head of Stransky-Kaischew Colloquium in department "Phase formation, crystalline and amorphous materials", IPC BAS. He has been at specializations in Germany, France and Russia. He is the co-adviser of a PhD student. In 2008, he received the prize "Acad. R. Kaischew" from the IPC for scientific achievements in physical chemistry. Associate Professor Dr. B. Rangelov is a representative of Bulgaria in the European Network on Crystal Growth 2015-2021 and member of the Executive Board of European Network on Crystal Growth. Since July 2020, he is Head of IPC BAS.

2. Description of the materials presented.

Assoc. Prof. Dr. B. Rangelov has submitted a list of 41 publications. Four of them are included in his PhD thesis. Another 8 are on the list of publications that are equivalent to habilitating work. (In my view, it is strange the NDCID's requirement for the last separation of papers in the absence of habilitating work.) More importantly, 25 out of 41 works are dated after the year he became an Associate Professor (2011), *i.e.* [17-41]. The majority of the publications, presented in the general list, are in reputable specialized journals: ***Journal of Physics: Conference Series*** (7), ***Journal of Crystal Growth*** (4), ***Comptes Rendus de L'Academie Bulgare des Sciences*** (4), ***Physical Review B*** (3), ***Surface Science*** (2), ***Crystals*** (2) and others. B. Rangelov is the first author in 11 and second in 6 publications. A list of 11 scientific projects, in which he is a participant and one, where he is the leader is presented. He is also a participant in 2 bilateral projects of IPC BAS (with the Institute of Physics of Semiconductors of SD of RAN and with AUTH Aristotle University,

Thessaloniki). As head of the laboratory of electron microscopy and microanalysis analysis, he contributed to attracting extra-budgetary funds for IPC BAS. The indices of the activity of Assoc. Prof. B. Rangelov go beyond the minimum requirements of IPC BAS for the scientific activity of the candidates for academic position "Professor". This is demonstrated in the table:

Metric Group	A	C	D	E	F
Minimum requirements	50	100	220	120	150
Activity of B. Rangelov	50	160	302	226	185

I accept all publications submitted as pertaining to the competition. However, in the review, I will focus on those, which contributions are substantial and/or B. Rangelov's participation is significant.

3. General characteristics of the applicant's scientific and scientific-applied research activities.

Based on the materials, presented and their grouping, made by B. Rangelov, I would rearrange the research with an element of gradation by importance on my part as follows:

1. Simulation and theoretical studies of instability on vicinal crystalline surfaces.
2. Monte Carlo simulation studies.
3. Electron-microscopic studies of two-dimensional nucleation, crystal growth and instability processes on vicinal crystalline surface Si(111).
4. Electron-microscopic studies of phase formation processes and characterization of different materials.

4. Basic scientific and applied contributions.

1.1. Instability type of waves of the steps density

The idea of crystal growth instability of vicinal crystalline surface with waves density of the steps was first addressed in two publications included in PhD thesis of B. Rangelov [7, 8], and then further developed in [10] and [29]. The experimental confirmation of such development is presented in [29]. In the four papers listed, B. Rangelov is the first author.

A vicinal crystalline surface with monatomic steps is considered, separated by smooth terraces. The process of growth/evaporation by moving steps, when their speed is high, is monitored. This means that there are no stationary conditions and the adatomic concentration on a terrace depends on the time. The evolution of the system of steps has been determined and the change of widths of the terraces between the steps has been studied. It is assumed that the concentration of adatoms on a terrace is constant on the entire terrace, but is influenced by the width of the terrace.

1.2. Grouping of steps on a vicinal crystalline surface

The conditions of instability, in which the steps on a model vicinal surface will not be at the same distance from each other, but will occur their grouping (the appearance of bunching) are considered. It is assumed that the difference in equilibrium adatomic concentration on both sides of

the steps is the cause of system destabilization [5, 12]. A relationship between the number of steps in a group, the width of the entire group and the time is displayed. Two hybrid models of step grouping are considered in [18].

1.3. Critical width of the terrace for transition from growth with movement of steps to two-dimensional nucleation

The transparency of steps and its impact on the transition from growth through movement of steps to growth with two-dimensional nucleation on the terraces has been considered. Growth by movement of steps occurs, when the temperature of the crystal surface is high enough and the free path of the adatoms is greater, than the average width of the terraces. The probability of the formation of a critical nucleus and the appearance of two-dimensional islands on the terraces as a new mechanism of growth increases as the temperature decreases. The type of growth at a given temperature is determined by the width of the terraces. The transition from one mechanism to the other takes place at the so-called critical width of the terrace for the given temperature. A general expression for the critical terrace width for step flow growth accounting for both the step permeability and the asymmetric incorporation of atoms to ascending and descending steps is derived. The two limiting growth modes are included: both diffusion, and attachment and detachment at high and low temperatures. The impact of step transparency is greatest in the average temperature range between kinetic and diffusion modes in "pure" form [6]. This work was included in PhD thesis and was subsequently cited 19 times.

2.1. Monte Carlo simulation studies of diffusion processes on vicinal crystalline surfaces and the impact of step transparency

The model considers a random atom migration along the square lattice. It is assumed that there is no re-evaporation or nucleation. When the atom reaches the step ledge, it can diffuse along it, separate from the step and return to the terrace, from which it came, or jump from the step and go to an upper or lower terrace. For each of these processes, some probability is set. It has been shown that in the absence of an external field or Ehrlich-Schwöbel barrier, there are symmetrical to zero terrace curves in the distribution of the number of jumps through the steps, higher and lower than it is. The main conclusion is that even if there is the transparency of the steps, the speed of movement of the steps should not be changed, because sooner or later all the adatoms will join one of the steps, even if it is not the first one they encounter [9]. B. Rangelov is the first author of this paper. It is cited 5 times.

The influence of an external field on the island's atoms has been studied, in order to preserve the integrity of a monatomic two-dimensional island on the surface. The introduction of an external field increases the probability of adatom diffusion in a given direction. The balance between the normal, lateral and external forces acting on the island's atoms also determines the critical values of the external field, at which the compact in form at the beginning island evolves [23].

The influence of the density of the kinks on the steps on their transparency is examined, taking into account the action of electromigration force. A model is proposed to explain the complex behavior of the phenomenon of step-grouping on a surface Si(111) depending on the direction of the electromigration force and temperature [24].

The change in the shape of the initially equilibrium two-dimensional islands or vacancy clusters was found, due to the directed action of the external electromigration force, causing diffusion of two-dimensional islands and vacancy clusters on a wall (111). In this simple model is set an infinite Ehrlich-Schwöbel barrier, that is, atoms cannot jump over steps [38].

2.2. Monte Carlo simulation studies of the thermal stability of metal nanowires

The thermal stability of one-dimensional monatomic nanowires, free-standing in space and without the stabilizing effect of the substrate, has been studied. Stability is impaired by the appearance of vacations, that is, the departure of atoms of more than one lattice parameter. This leads to the appearance of holes, after which the chain breaks down [28].

The stabilizing effect of the substrate is taken into account in two-dimensional homoepitaxal chains of atoms. These are several side-by-side one-dimensional chains on a surface (111). Under the action of thermal fluctuations, the tear mechanism passes through thinning of the strip to the formation of a section with a one-dimensional chain. This is how vacations are formed, but can be refilled. If a "hole" in the strip cannot be filled, a rupture and disintegration of the strip occurs [35].

2.3. Monte Carlo simulation studies of particles with anisotropic interactions and diffusion-controlled growth in a two-particle system

To the familiar model of diffusion-controlled aggregation, a sticking coefficient to the growing two-dimensional cluster is added. This shifts the process from diffusion-controlled to kinetically-controlled. A model of diffusion limited aggregation is presented in the presence of two types of particles (A and B). A type particles are deposited/aggregated only to A and B type are deposited only to B [19].

Polymorphic forms of protein crystals can undergo transitions in the process of growth. With the help of a two-dimensional Monte Carlo simulation, interactions between model molecular complexes that are not spatially symmetrical are considered. Spontaneous polymorphic transition depends on the chosen order of protein particles "patches". The transition is feasible in a narrow temperature range, depending on the force connecting "patch" to "patch" [39].

3.1. Two-dimensional nucleation, crystalline growth (multilayer island and spiral) and critical width of terraces on a vicinal crystalline surface

Using advanced electron-microscopic technique REM and LODREM (Low Distortion Reflection Electron Microscopy) in France, the distance between two successive steps in spiral growth (or evaporation) in conditions of supersaturation and undersaturation on the surface Si(111) has been examined. It has been found that, for both the case of growth and the case of evaporation, a reverse proportional exponent relationship between the distance of two adjacent steps of the Archimedes spiral and the supersaturation was obtained. The scale exponent in this dependency is between 1/3 and 1/2. This confirms the overlap of diffusion fields on adjacent steps due to the large free path of the adatoms for the corresponding high temperature interval [4]. This work is included in PhD thesis. It was cited 9 times.

A link has been established between theoretical simulation studies [6, 9] with experimental results obtained with UHV REM [16, 20, 27]. For this, an experimental technique in Russia is successfully used. The focus is the critical terrace width, at which transitions from growth by moving steps to growth with two-dimensional nucleation on the terrace of a vicinal crystal surface Si. The value of the exponent is determined, which gives the ratio (scaling) between the critical terrace width and the value of the incoming flux of adatoms. From it is determined the size of the critical nucleus, as well as the activating energies for two-dimensional nucleation at intervals below and above 720°C. In connection with the theoretical and simulation results of [6], the energy barrier for embedding adatom in the "lower" step of the terrace has also been determined.

3.2. Instability on vicinal crystalline surface Si(111) – waves of the density of the step

The existence of a new type of instability in vicinal growth has been found through theoretical analysis and experimental REM and LODREM technique in France. There is definitely a critical speed of the steps, which has a significant role to play in determining the criterion of stability. At large incoming flux of adatoms, high speed of step movement in kinetic mode, *i.e.* rapid diffusion of the adatoms on the surface and the slow attachment or detachment of the adatoms to/from the steps, the growth will be unstable, even when there is no destabilizing factor. Appropriate experimental conditions for the appearance of waves of the steps density have been selected. Thus, it has been shown that, when the movement of the steps is very fast, the quasi-static approximation of Burton-Cabrera-Frank's theory of crystalline growth and the non-stationary effects of crystallization kinetics are not valid [29]. In this theorist-experimental work, B. Rangelov is the first author.

It is clear from what has been said so far that simulation and theoretical studies are combined with experimental proofs (sometimes in one work). This is a very good illustration of the essence of B. Rangelov's contributions as a theorist and experimenter.

4. Electron-microscopic studies of phase formation processes and characterization of different materials.

In this section the contribution of B. Rangelov as a co-author in complex studies, involving various methods, carried out mainly with colleagues from IPC BAS are considered. They illustrate his ability to work with different collectives on diverse topics.

B. Rangelov cooperates in the preparation of thin layers of CdS on a conductive substrate [1]. This work was subsequently cited 22 times.

The electrodeposition of copper in layers of polyaniline (PAN) in various redox state has been investigated. Electrochemical studies are combined with data, obtained with SEM and XPS. It has been shown that the deposition processes and characteristics of metal polymer composites depend on the homogeneity and redox state of the polymer [3]. This is the most cited work - 40 times. The author's report under [3] describes another paper, namely [2].

In order to replace platinum for catalysts for HER/OER reactions, Ebonex (non-stoechiometric TiO_2) is first mechanically treated for different durations in order to increase the active area. Then, by sol-gel method it is doped with cobalt. The morphology of the Co-Ebonex

catalysts was investigated using TEM and SEM, and electrochemical behavior with cyclic voltemperometry and galvanostatic method [13]. In another work, again with colleagues from Faculty of Technology and Metallurgy of the University in Skopje, TiO_2 nanoparticles were prepared, using titanium tetraisopropoxide (TTIP) as precursor. The change in the crystal state was tracked depending on the subsequent thermal treatment. TGA/DTA, XRD and Raman spectroscopy were used. The size and shape of the nano-formations were observed with TEM, and the morphology of TiO_2 aggregates was investigated with SEM [26]. B. Rangelov's participation in these two works is related to the electron-microscopic part. The paper [13] has been quoted 22 times and [26] - 6 times.

An important and in my opinion a significant part of the research was carried out in cooperation with the glass and glass-ceramic group at IPC BAS. They address the problem of the treatment of specific waste raw materials after processing in an incinerator and use a no small part (up to 60%) to obtain sintered glass-crystal materials. The possible positive environmental impact of these studies should be emphasized also. After receiving the so-called frits (glass powder/grains), they are pressed and sintered in different temperature modes, namely heating speeds and temperature retention steps. After separating grains of specified medium or maximum size, different output fractions may also be used. Particular attention is paid to the formation of so-called open and closed porosity and their dependence on the speed of heating. B. Rangelov's contribution is mainly in electron-microscopic research [14, 15, 17, 25]. The work [17] has been cited 37 times.

The production and characterization of glass-ceramics derived from metallurgical waste of the steel and ferronickel manufacture has been considered in [30, 36]. The processes of nucleation were studied and the optimal temperature was determined, as well as retention times for the preparation of a crystalline phase. The formation of crystallization-induced porosity in volumetric crystallization in this type of glass-ceramic has been shown. It has been established that the basic structure of glass ceramics derived from the waste from of the ferronickel production is the result of the bimodal liquid-liquid immiscibility. This leads to the creation of a very fine crystal magnetite phase. It serves as the basis for the growth of the main pyroxene phase in the material.

5. **Reflection of the scientific publications of the applicant in Bulgarian and foreign literature.**

The documents present a list of 198 citations by foreign authors. I found 50 more citations, which are mainly from 2019 and 2020, as well as from doctoral dissertations. Most of these theses are defended in prestigious universities: Imperial College, UK (2); University of California Berkeley, USA; University of Southampton, UK; Universität zu Köln, Deutshland; Linköping University, Sweden; Universite de Grenoble, France; Nanyang Technological University, Singapore; Technische Universität, Darmstadt, Deutshland, a patent and others. In my opinion, these citations are no less prestigious than those in scientific journals are. The most cited are experimental works: [3] – 40 times, [17] – 37 times, [13] – 22 times, [1] – 22 times. The theoretical work [6] has been cited 19 times.

6. Critical notes and recommendations to the applicant's scientific papers.

I definitely think, the author's report could have been written better. I would like to give an example to that. The contemporary trend in shaping such texts implies the introduction of new

paragraphs often enough, which helps to perceive content comprehension. For example, on page 13 there is not a single new paragraph. The text would benefit from shortening and laconism of sentences.

7. Personal impressions of the reviewer about the candidate.

I know Associate Professor Dr. B. Rangelov as a colleague of IPC BAS. He is distinguished by his modesty, focus and diligence in his scientific work, to which he is fully dedicated. As Head of the laboratory of electron microscopy and microanalysis, he made great efforts it to perform its functions and personally participated in the maintenance of the apparatus.

CONCLUSION

The documents presented by Associate Professor Dr. Bogdan Stavrev Rangelov, the only candidate in the announced competition for professor at IPC BAS, correspond to the topic in scientific specialty "Physical Chemistry", fully satisfying the requirements of the National Low, its Regulations and Regulations for its application of IPC BAS. The candidate's contributions are clearly distinguishable. The analysis of his overall scientific-research work and scientific-organizational activity, as well as my personal impressions, give me reason to believe that Associate Professor Dr. Bogdan Rangelov possesses the necessary professional qualities and achievements to be elected in the academic position "Professor" at the Institute of Physical Chemistry of BAS.

Date 18.08.2020

(Prof. Dr. Stephan Armyanov)