REVIEW

in a competition for a professor in a professional field 4.2. Chemical Sciences, for the scientific specialty "Physical Chemistry" announced in the State Gazette in number № 20 dated 10.03.2020 with candidate Assoc. Prof. Dr. Bogdan Stavrev Ranguelov

Reviewer: Assoc. Prof. Dr. Dragomir Mladenov Tatchev

1. General provisions and brief biographical data of the applicant.

The Laboratory of Electron Microscopy and Microanalysis of IPC-BAS is a key element of the structure of the Institute of Physical Chemistry and participates in the implementation of research activities in almost all scientific tasks and thematic areas. It has always been closely related to the study of the processes of nucleation and growth of metal and alloy crystals on various supporting substrates, epitaxial growth of semiconductors, morphological stability of inorganic crystals, etc., which are part of the main scientific topics of the Institute. The scientific interests of the candidate, Assoc. Prof. Dr. Bogdan Ranguelov, who is a longtime member of the laboratory first as its associate and later as head naturally gravitate to these topics.

Bogdan Ranguelov graduated from Sofia Mathematical High School, majoring in physics in 1988, after which he entered the Faculty of Physics at Sofia University "St. Cl. Ohridski". He graduated with a master's degree in physics in 1995. His employment with the Institute of Physical Chemistry began in the same year. In 2009 he received the educational and scientific degree (ESD) "Doctor" with a dissertation on "Instability of vicinal crystal surfaces - grouping of steps." Since 2011 Bogdan Ranguelov has been an associate professor at IFH-BAS. Since 2010 he has been the head of the Laboratory of Electron Microscopy and Microanalysis.

Associate Professor Ranguelov also had the opportunity to gain international experience in his specialization at the Friedrich-Alexander University in Erlangen, Germany in the period 2000-2004, where he studied the molecular reactions of the surface and catalytic properties of crystalline surfaces Pt (111) and Fe (100) using HREELS (High resolution electron energy loss spectroscopy) spectroscopy. Subsequently, he maintained collaborations and made short-term visits to the Center Interdisciplinaire de Nanoscience de Marseille CINaM, Marseille, France and the Institute of Semiconductor Physics SO-RAS 2010, Novosibirsk, Russia, where he studied growth processes on the Si crystal surface (111).

As of today (August 28, 2020), 42 articles by Assoc. Prof. Ranguelov can be found in the Scopus database. His Hirsch index is 8 without taking into account the self-citations of all co-authors. Associate Professor Ranguelov is also a co-author of a patent for an invention.

2. Description of the submitted materials

For the acquisition of the position of "professor" Assoc. Prof. Ranguelov has submitted a total of 41 articles, 23 of which are not included in the dissertation for the educational and scientific degree "Doctor" and are not presented for the position of "Associate Professor". Of all the submitted articles, 16 are in international scientific journals with rank Q1, 10 - Q2, 9 - Q3, 2 - Q4, one paper is in a journal without impact factor but with SJR, three articles are published in full in conference proceedings. Of the articles not repeating those submitted for receiving ESD “doctor” and the position of "associate professor" 9 are in journals with rank Q1, 7 - Q2, 5 - Q3, 1 - Q4 and one in a magazine without impact factor but with SJR. The calculation of the points according to the ranks of the journals and the distribution given by the candidate in the "Information on the fulfilment of minimum requirements of the Institute of Physical Chemistry" Acad. R Kaishev"- BAS" is shown in Table 1.

In the provided by the candidate "Information for fulfilment of minimum requirements of the Institute of Physical Chemistry "Acad. R Kaishev"- BAS for the scientific activity of the candidates for the academic position" professor "in District 4. Natural sciences, mathematics and informatics, 4.2. Chemical Sciences "lists 113 citations, which carry 226 points, with a requirement of 120 points. A reference in the Scopus database to date (28.08.2020) shows the presence of 212 citations (424 points) without taking into account the self-citations of any of the co-authors. Without a thorough check of the citations, it is clear that the criterion of 120 points for group E is overfulfilled.

A reference in the SONIX system for scientific reporting at the Bulgarian Academy of Sciences confirms the participations in research and educational projects presented by Assoc. Prof. Ranguelov, which brings him 160 points in group E. Assoc. Prof. Ranguelov was also co-supervisor of a successfully defended doctoral student Alexandra Stefanova Kamusheva so he gets additional 25 points.

Table 1 shows the compliance of the points achieved by Assoc. Prof. Ranguelov with the minimum national requirements, the requirements of BAS, as well as the requirements set by the Scientific Council of IPC according to Annex № 1 of the Regulations on the terms and conditions for obtaining scientific degrees and occupying academic positions at the Institute of Physical Chemistry "Acad. R. Kaishev" at the Bulgarian Academy of Sciences. It can be seen that Assoc. Prof. Bogdan Ranguelov exceeds both the national and the requirements of BAS and IPC-BAS for holding the academic position of "professor". Quantitative indicators of the criteria for holding the academic position are met.

Table 1 Points achieved by Assoc. Prof. B. Ranguelov in comparison with the national requirements, the requirements of BAS and the Institute of Physical Chemistry of BAS

Group of indicators	National requirements	Requirements of BAS	Requirements of IPC-BAS	Points scored
A	50	50	50	50
Б	-	-	-	-
B	100	100	100	160
Г	200	220	220	302
Д	100	120	120	226
E	150	150	150	185

All submitted works are relevant to the competition. The review will reflect the most important of them, in which Assoc. Prof. Ranguelov has the most significant contribution.

3. General characteristics of the research and applied research activity of the candidate.

The most significant works of the research activity of Assoc. Prof. Ranguelov combine simulation and theoretical research [5, 6, 7, 8, 9, 10, 12,18, 23,24, 29, 38] with electron microscopic observations of processes. of phase formation in condensed matter. It is worked exclusively on a vicinal crystal surface. The research is fundamental in nature, as it examines the phase formation at the level of addition and separation of individual atoms - a method representing the best achievements of the Bulgarian school of physicochemistry. On the other hand, microscopic observations were performed on the vicinal Si surface (111). Silicon is still the most widely used material in microelectronics, which is why knowledge of growth and epitaxy on a silicon crystal is essential. There is also a shift to Monte Carlo simulation studies, both on vicinal surfaces [9, 23, 24, 38] and on metal nanochains [28, 35] and on model systems of two types of particles [39, 19].

The second essential part of the works presented by Assoc. Prof. Ranguelov is a broad-spectrum bouquet of scientific topics, in which the candidate quite successfully fits in with a well-defined contribution. These are the areas: glass and glass-crystal materials [14, 15, 17, 25, 30, 32, 36, 40], soft condensed matter [22, 37], thin films and catalysts. [1, 2, 3, 11, 13, 21, 26, 31, 33, 34, 41], as the unifying factor are again electron microscopic studies of phases of formation and characterization. This shows Assoc. Prof. Ranguelov as a well-established specialist who masters his methodology to perfection and can easily apply it in various fields.

4. **Main scientific and scientific-applied contributions.**

As an extremely good achievement I would point out the theoretical justification for the presence of instability on the vicinal crystal surface in the form of waves of step density [7, 8, 10], the subsequent experimental development [16,20,27] and its experimental confirmation [29]. It should be noted that the four most important articles Assoc. Prof. Ranguelov is the first author, which undoubtedly speaks of a major contribution to the study.

The study is based on finding a non-stationary solution of the equations for the motion of steps on a (1+1)D vicinal crystal surface, in contrast to the quasi-stationary solutions used so far. Theoretical considerations [7, 8, 10] solve the problem of crystal growth on the vicinal surface if the speed of movement of the steps is so high that it cannot "provide" the conditions for stationarity - ie. the value of the adatomic concentration on a given terrace begins to depend on time and not only on the coordinate, as in the stationary solution of the diffusion equation. Since the diffusion equations are of the second kind, the premise of a kinetic regime is used, in which there is a rapid diffusion on the terraces and therefore the concentration of adatoms on the terrace is constant. Theoretical and simulation studies predict that under certain conditions in the kinetic regime of rapid diffusion of adatoms on the surface and slow attachment or detachment to and from the steps, growth will be unstable. Instability manifests itself as waves of step density. Another instability of growth on the vicinal surface is the grouping of the steps - ie. the system of equidistant terraces breaks up into bunches of very wide and very narrow terraces. It is shown that such instabilities can occur in the absence of any external destabilizing factors, but only due to the effects of nonstationarity.

The article [29], of which Assoc. Prof. Ranguelov is also the first author, is a summary of the theoretical discoveries and their experimental confirmation by reflection electron microscopy (REM). The main contribution here is both in the confirmation of the theoretical researches and in the finding of experimental conditions for observations of the waves of the density of the steps in a complex experiment under electron microscopy. Finding experimental conditions for observing and proving this new kinetic instability requires finding out conditions in which there are no destabilizing factors and at the same time the use of reflecting electron microscopy equipment, which is the only possible observation of monatomic steps in conditions of growth or evaporation. The research was carried out on a vicinal crystal surface Si (111), on which the research of Assoc. Prof. Ranguelov has traditionally been carried out. By means of REM, studies have been carried out in an appropriate temperature range and direction of direct current, which shows the initial stages of the formation of waves of density of steps in conditions of growth. The observed density waves "exist" as long as the corresponding value of the incident flow can be provided, providing a supercritical value of the movement of the steps, at which the non-stationary effects begin to appear.

The step bunching in a non-stationary solution of the BKF model in kinetic mode was studied in [7], and the conditions were discovered under which we have an unstable solution of the system that is called the "kinetic effect of memory" on the widths of the terraces. A linear analysis of the stability is made by the method of Fourier perturbations of the system of equations and expressions are obtained for the critical velocity of the steps above which the system of steps is unstable, ie. small deviations from the equilibrium positions of the steps will become larger. 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. The considered model is complicated [8] by the addition of electromigration force - the force that acts on the adatoms on the surface of the crystal if a direct current flows through the crystal. It has been established that when 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 the terraces and due to the influence of electromigration. At the direction of the electromigration force down the steps and above the critical value, the classical grouping of steps (bunching) is observed, while at a lower value waves of density are observed for both the case of growth and the case of evaporation. It is the problem of "separating" these two destabilizing factors from each other that lies in the idea of experimental research in [29]. The degree of complexity of the model is increased by taking into account the influence of the transparency of the steps - this means that the speed of a step at a given time will depend on processes that occurred on adjacent steps in previous moments [10]. This "non-local" dynamics of the steps is studied in [9] by the Monte Carlo method. It has been found that the vicinal wall with transparent steps is unstable when the drift velocity of the adatoms multiplied by the relative change of the adatomic concentration relative to the equilibrium is greater than the critical velocity for the movements of the steps. The relationship between the number of terraces involved in the wave of instability and the relative transparency of the steps is also obtained.

The step bunching on a vicinal crystal surface is represented in several other works by Assoc. Prof. Ranguelov [5,12,18], and in one of them he is the first author. They use BKF-type equations, with different model parameters on or off, with the aim of finding the instability conditions under which the steps would be grouped. The scaling relations between the size of the groups of steps, the width of the whole group and the time are obtained. The models manage to explain some of the characteristics of the significant variety of experimentally observed grouping of steps.

The works [6, 9] focus on the question of the transition from growth through movement of steps to growth through two-dimensional nucleation on the terraces at constant temperature. It was found that this transition depends on the width of the terraces of the vicinal surface and a critical width has been established, above which the growth passes into the mode of nucleation. A generalized expression for the critical width of the terrace for growth by movement of steps is obtained, taking into account the asymmetry of the kinetic coefficients and transparent steps. An Arrhenius dependence of reducing the critical width of the terrace with decreasing temperature was obtained, as the dependence itself represents a smooth transition between two lines with different slopes, corresponding to the two boundary cases of growth - diffusion and kinetically limited. An assessment was made when the influence of the transparency of the steps is greatest - in the average temperature range between the "pure" kinetic and diffusion regimes.

The next cycle of works with significant scientific contribution concern the homoepitaxy on vicinal crystal surface Si (111) [16, 20, 27], and use the theoretical consideration in [6, 9]. In the last two works Assoc. Prof. Ranguelov is again the first author. The main subject of research is the so-called critical width of the terrace, in which there is a transition from growth through the movement of steps to growth through two-dimensional nucleation on the terrace. It was found that homoepitaxial growth is multilayered, multi-embryonic and manifests itself as the formation of dynamic pyramidal structures having spatial and temporal periodicity. A surface temperature value of 720 ° C was found, below which crystal growth takes place by means of a kinetically limited mode of adatoms attachment to the steps. Accordingly, at temperatures above 720 ° C the growth takes place by diffusion limited mode. The value of the power indicator, which gives the ratio between the critical width of the terrace and the value of the falling flow of adatoms, was determined, and the size of the critical embryo was determined, as well as the activating energies for two-dimensional nucleation in the intervals below and above 720 ° C.

Using the same experimental and theoretical approaches, the "transparency" of the steps [27] of the vicinal crystal surface and its influence on the surface growth regimes was studied. In this case, Si (111) terraces with widths from 1 to 100 micrometres, separated from each other by grouped monatomic steps, were used as a surface base.

As a result, it is shown that in the temperature range 600 - 750 ° C the continuous two-dimensional nucleation and subsequent growth lead to the formation of elongated pyramidal ridges (at T <720 ° C) and to individual pyramids at T = 750 ° C, both a manifestation of growth instability. It was found that the change in the width of the upper terrace of the pyramidal forms of growth, as well as the increase in the number of layers involved in the pyramidal forms, are related to the size of the critical embryo and the predominant flow of adatoms down the steps at a temperature of 650 ° C. However, at temperatures above 720 ° C, a predominant flow of adatoms up the steps is established due to the higher Ehrlich-Schöbel barrier for incorporation in the upper standing step. Thus, in [27] the relations between the growing conditions, the transparency of the steps of the vicinal surface and the morphology of growth are established.

Research on the growth of a vicinal crystal surface is complemented by Monte Carlo simulations concerning the diffusion of adsorbed atoms. It was found that when varying the parameters of the model such as the density of kinks on the steps, or the probability of diffusion on the rim of the steps, in all cases, on average, one adatom visits up to 10 steps in the vicinity of the terrace from which he began his diffusion after falling from the gas phase [9]. It has been 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.

It has been experimentally proved that for the Si (111) surface there are three consecutive temperature intervals in which the grouping of steps and the stable growth alternate. Within the BKF model, this "switching" from stable to unstable and back to stable growth can be explained only if the existence of the phenomenon of transparency of the steps in the average temperature range is allowed. Monte Carlo simulations [23] offer a new hypothesis to explain this phenomenon. Simulations of a two-dimensional island on a terrace with (111) orientation clearly show three modes of disintegration of the island depending on the magnitude of the applied electromigration force. These three modes, together with the transparency of the steps, are associated with the complex experimental behaviour of the steps bunvhing.

The scientific contributions of Assoc. Prof. Ranguelov listed so far concern a fundamental scientific field related to the growth of crystals. The Burton-Cabrera-Frank model for the nonstationary case was further developed, which led to the enrichment of existing knowledge and theories. The conditions and limits of the different growth regimes of a vicinal crystal surface, stationary, ie. with equidistant terraces, non-stationary - of the type of grouping of steps or waves of the density of the steps or by two-dimensional nucleation. The wave density regime of the foot density was predicted and subsequently experimentally established. All theoretical developments are closely related to electron microscopy experiments, in which Assoc. Prof. Ranguelov is a specialist. In a significant part of the publications Assoc. Prof. Ranguelov is the first author, which confirms his significant personal contribution.

I believe that the scientific contributions presented so far are sufficient for awarding the candidate the academic position of professor in a professional field 4.2. Chemical sciences. Therefore I will not dwell on his contributions in the field of electron microscopic studies of the processes of phase formation and characterization of glass and glass-crystal materials [14, 15, 17, 25, 30, 32, 36, 40], soft condensed matter [22, 37] and thin films and catalysts [1, 2, 3, 11, 13, 21, 26, 31, 33, 34, 41]. They only show the wide range of knowledge and skills of the candidate, which is a significant plus in modern scientific interdisciplinarity.

5. Response to the scientific publications of the candidate in Bulgarian and foreign literature.

In the documentation the candidate presented 198 citations. The reference in Scopus to date gives 212 citations without the self-citations of all authors. It is known that Scopus and the Web of Knowledge usually give a reduced number of citations, in particular omitting citations from dissertations. The most cited are the applied works of Assoc. Prof. Ranguelov, in particular, related to the study of glass and glass-crystalline materials in order to secure industrial waste. What follows is generally the work related to the crystal growth of the vicinal surface, with the number of citations varying between 3 and 16 citations per article. The most cited article is [6] - 16 times. It can be concluded that the works of Assoc. Prof. Ranguelov are well accepted in the scientific literature.

6. Critical remarks and recommendations to the scientific works of the candidate.

The update of the main topic of the candidate may be relatively slow.

7. Personal impressions of the reviewer about the candidate.

I have known the candidate for more than 20 years and I have witnessed his career growth, although we have not had the opportunity to work together on a common task. Assoc. Prof. Ranguelov is a diligent scientist, with a sense of detail and its refinement. Over time, he gained international experience, both as a research participant and as a scientist who can clearly and attractively present scientific results to a wide audience. Assoc. Prof. Ranguelov is a collegial, correct and non-conflicting person, enjoying trust and authority among colleagues. Last but not least, as the head of the electron microscopy laboratory of IPC, Assoc. Prof. Ranguelov gained some managerial and scientific-organizational experience.

Conclusion

According to the submitted documents, the only candidate in the announced competition for a professor at IPC-BAS, Associate Professor Dr. Bogdan Stavrev Ranguelov meets the requirements for holding the academic position of professor in a professional field 4.2. Chemical Sciences, specialty "Physical Chemistry", satisfying and exceeding the requirements of ZRASRB, the Regulations for its application in the Republic of Bulgaria and the Regulations for its application in IPC-BAS. The candidate's contributions are clearly distinguishable and indisputable. The analysis of his overall research work and scientific-organizational activity, as well as my personal impressions, give me reason to recommend to the members of the scientific jury for the competition to support the candidacy of Associate Professor Dr. Bogdan Ranguelov to be elected to the academic position of "Professor" for the needs of Laboratory "Electronic microscopy and microanalysis "at the Institute of Physical Chemistry of BAS.

Date: 15 September 2020

Reviewer

/ Assoc. Prof. Dr. Dragomir Tatchev /